RECOVERY OF VALUE ADDED FUELS FROM WASTE POLYOLEFINS/ BICYCLE TYRE AND TUBE

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CERTIFICATE

This is to certify that the thesis entitled "Recovery of value added fuels from waste polyolefins/ bicycle tyre and tube", being submitted by Ms. Debalaxmi Pradhan (Roll No. 609CH304)has been carried out under my guidance in partial fulfillment of the requirement for the degree of Master of Technology (Res.) in Department of Chemical Engineering, National Institute of Technology Rourkela and this work has not been submitted elsewhere for a degree.

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(Debalaxmi Pradhan)

CONTENTS

CHAPTER 3

CHAPTER 4

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Thermal pyrolysis is one of the renewable technologies where waste tyre and tube were pyrolysed into fuel oil, carbon black, and combustible gas under the action of reasonable technological conditions. This technology could not only reasonably and effectively dispose waste tyre and tube without pollution, but also is effective in producing fuel that can reduce energy crisis. In the present work, thermal pyrolysis of waste bicycle tyre and tube samples were carried out in a semi batch reactor made up of stainless steel within the temperature range of 450ºC to 800ºC. The optimum pyrolytic oil of 49.6%was obtained at 600ºC for tyreand 49.65% for tube at 700ºC. Again to increase further oil yield, different catalysts have been used i.e.SiO_2/Al_2O_3, Kaolin, CaO, and MgO. But, it was identified that the catalytic pyrolysis was not effective when compared to thermal pyrolysis in terms of product yields (oil).The physical properties of the oil obtained were determined by using standard test methods and the chemical composition was analyzed by using FTIR, GC-MS analyzer. The char obtained was characterized for its calorific value and surface morphology by SEM. Characterization of both pyrolytic oil shows that the obtained oil is a mixture of diesel and gasoline. The composition of the oil showed the presence of aromatic and aliphatic compounds. Kinetic parameters of tyre and tube sample were also studied at the heating rates of 10, 15and 20ºC/min by TGA which showed that with the increase of rate of heatingactivation energy decreases. Engine performance test was done by using different blends such as 10%, 20%, 30%, 40% and 50% of bicycle tubepyrolyticoil with diesel. Performance, emission and combustion characteristics of the diesel engine were studied. From engine test it was concluded that 40% blend of tube pyrolytic oil with diesel can be substituted with diesel. After proper treatment these oil can be used as substitute of alternative fuel.

CHAPTER 1

1. Introduction

1.1 Origin of the study

Energy crisis and environmental degradation are the main problems that mankind is facing now a days. This is due to the growing population, rapid industrialization and disposal of diverse solid wastes, which are generated on a regular basis. To solve this energy crisis and environmental degradation, scientists are putting much effort on the potentials of utilizing appropriate technologies to recover energy and useful by-products from domestic and industrial solid wastes. Thus considerable research has been done to recover energy from waste materials, including materials that are not bio-degradable. Such materials include biomass, municipal solid wastes, industrial wastes, agricultural wastes and other low grade fuels as well as high energy density materials such as rubber and plastics. Rubber containing wastes such as tyre and tube waste are causing a big environmental problem because it is an artificial polymer and also not biodegradable. Rubber containing waste takes significantly much longer time as compared to biomass materials in case of photo degradation.

There is a predominant increase in tyre and tube wastes due to phenomenal increase in number of vehicles within India. The statistical data of production of tyre and tube can be known from the Indian Rubber Industry, at a Glance 2011. In India, the production of tyre increased from 66032 metric tonnes to 97137 metric tonnes from 2005-06 to 2009-10. Similarly the production of tube increased from 53421 metric tonnes to 81448 metric tonnes from the year 2005-06 to 2009-10.According to this data the production of tyre is forecasted to increase and this indicates that at the same time the annual disposal of waste tyre volume will increase at the same rate as new tyre is manufactured [1].

These discarded wastes pose a threat to the environment and human health if not handled properly. Thus timely action regarding recycling of used tyres is necessary to solve the problem keeping in view the increasing cost of raw material, resource constraints and environmental problems including fire and health hazards associated with the stockpiles of the used tyres.

Therefore, Pyrolysis is an interesting and challenging area of research. Besides that, pyrolysis of tyre waste has several advantages that can help resolve the energy crisis. So a number of studies have been conducted to investigate the pyrolysis of waste tyres in both laboratory and industrial scale, under either inert or partial oxidizing atmosphere and maybe optimized to produce high energy density oils, solid char and gases. In addition to that, the oil products can be stored until required or readily transported to where it can be most efficiently utilized [2].And it is well-known that waste tyres possess high volatiles and low ash content, with a heating value that is greater than that of coal and biomass. So waste tyre can be a source of energy and valuable chemical product, and their thermal decomposition makes the recovery of useful compounds possible. Conventional methods for tyre shredding and metal separation, allows seamless incorporation of this technology for oil production and waste tyre disposal. Therefore in recent years there has been an increased interest in production of oil fuel from waste tyre by pyrolysis method. This innovative technology, because of its portability and scalability, uniquely address the challenges faced when converting tyres to low sulfur oil [3].

1.2 Problem statement

In general, there is a lack of awareness and concern among the industry in particular and the public in general on the environmental and health impacts due to improper management of waste tyres in India. The major chunk of these environmentally associated problems takes place because of the lack of a formal, well-coordinated management system for waste tyres. Thus, the disposal of vehicle tyre and tube represents a major environmental issue throughout the world.

For many years landfill was the main practical means for dealing with the problem of waste tyre. However the practice is rapidly declining as tyres do not degrade easily in soil as they are bulky, taking up valuable landfill space and prevent waste compaction. Open dumping is another method of disposing the waste tyres. It also has many hazardous effects on the environment. For an example when it results in an accidental fire, it causes a great deal of environmental pollution and most of the time it also pollutes the soil and contaminates underground water. So far today, waste tyres have been mainly dumped in massive stockpiles, which provided ideal breeding grounds for disease carrying mosquitoes and other vermin [4].

The utilization of these waste materials is indeed an important option for checking the economic and environmental concerns of the modern society which develops with the growing production and utilization of tyres across the world [5]. As every tyre is destined to go as waste stream for disposal/recycling/reclamation, despite its passage through retreading process, the number of used tyres being discarded is going to increase significantly. Timely action regarding recycling of used tyres is necessary in view of solving the problem of disposal, increasing cost of raw material, resource constraints and environmental problems including fire and health hazards associated with the stockpiles of the used tyres. The problem has drawn attention of planners, environmentalists, consumers and industry in the developed countries like the countries of Western Europe, USA, Japan, Australia etc. where billions of used tyres are stock piled. These stockpiles are also direct loss of energy and resources in addition to fire and health hazards and other environmental issues [6]. Further incineration was studied for the thermal treatment of waste tyres, because it involves combustion of waste at highly controlled temperatures. There are various general public concerns regarding the health consequences of incineration of wastes because incineration of the tyre waste emits a lot of toxic compounds such as dioxin, mercury, cadmium, nitrous oxide, hydrochloric acid, sulfuric acid, fluorides and particulates that can be

inhaled and magnify or stay permanently in our lungs. They can cause an array of dieses like asthma and cancer. It is known that heavy metals like arsenic, lead, mercury, chromium and organic chemicals such as polycyclic aromatics hydrocarbons, dioxins and furans, radioactive materials are not destroyed by incineration [7].

Moreover, different techniques are used for tyre recycling such as retreading, reclaiming, incineration, grinding, etc. which have significant drawbacks and limitations [8].A possible solution to overcome tyre and tube waste problems would be pyrolysis which has currently received renewed attention from the research organizations. Pyrolysis basically involves the decomposition of the wastes at high temperatures (300-900°C) in an inert atmosphere. Three major products are typically obtained from the organic solid wastes, such as oil, solid char and gases. The pyrolysis of waste tyre has a number of advantages as a treatment option since the derived oils may be used directly as fuels or added to petroleum refinery feed stocks. They may also be an important source for refined chemicals. The derived gases are also useful as fuel and the solid char may be used either as smokeless fuel, carbon black or activated carbon. Pyrolysis is the economical reuse of materials from wastes like tyres to obtain improved products and energy. Their high volatile nature, carbon contents and higher heating value makes them excellent material for energy recovery with the appropriate technology [9].

1.3 Research Objective

In this study, bicycle tyre and tube waste have been used as raw materials for pyrolysis process. The different objectives are summarized as:

1. To obtain liquid fuel from bicycle tyre and tube waste by thermal pyrolysis.
2. To characterize the liquid fuel for their physical properties and chemical composition.
3. Characterization of solid residue by using different analysis such as SEM, proximate and ultimate analysis.
4. Kinetic study of thermal pyrolysis for tyre and tube.
5. Engine performance and emission analysis by using different blends of diesel with tube pyrolytic oil.

1.4 Thesis outline

Chapter 1 Introduction part

Chapter 2 A literature reviews is presented on what polyolefins are, chemical structure of different rubber, and different recycling process to recover the valuable products.

Chapter 3 Materials and Methods, characterization procedure for raw material, experimental method for pyrolysis process and analysis of liquid product obtained in pyrolysis process.

Chapter 4 Represents the result and discussion part, in which explanation regarding Thermogravimetric analysis of materials, the thermal and catalytic pyrolysis at different temperature range and the composition of liquid product, fuel properties were given.

Chapter 5 Kinetic study explained the detail calculation of kinetic parameters by using first order.

Chapter 6 This chapter discusses the detail engine performance test of liquid fuel blending with diesel which includes performance characteristics, emission characteristics, and combustion characteristics.

Chapter 7 Provides the conclusion based on the experiments conducted and gives some recommendation for further research that can be conducted in this area.

CHAPTER 2

2. Literature Review

2.1 Polyolefins

Polyolefins are one type of synthetic resin produced by the polymerization of olefins or alkenes (molecules with the general formula (C_nH_{2n}) such as ethylene, propylene, butene, isoprene, pentene, etc. The name "olefin" means oil-like and refers to the oily character of the materials. Polyolefins may have many applications. Polyolefins is the most widely used plastic and in tonnage terms olefins elastmores such as styrene-butadiene copolymers has a dominant application in making of tyre and tube. The chemical structure of the olefin can be represented as Fig-2.1.

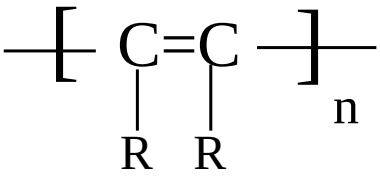


Fig-2.1 Chemical structure of olefin

2.2 Different types of rubber used in tyre and tube

Rubber is a versatile product with various usages. It is grown in various countries worldwide and plays a crucial role in the Indian economy too. India is one of the leading producers of rubber in the world. India is fourth largest producer of natural rubber next to Thailand, Indonesia and Malaysia [1]. The growth of the industry and importance of rubber goes hand-in-hand. It is a known fact that 75% of rubber produced in the world is used in the production of tyre [10].From the Fig 2.2 and Fig 2.3 it has been observed that the production of tyre and tube has been increased year wise [1]. Three major categories of rubber are used for tyre and tube making. They are namely natural rubber, synthetic rubber and reclaimed rubber.

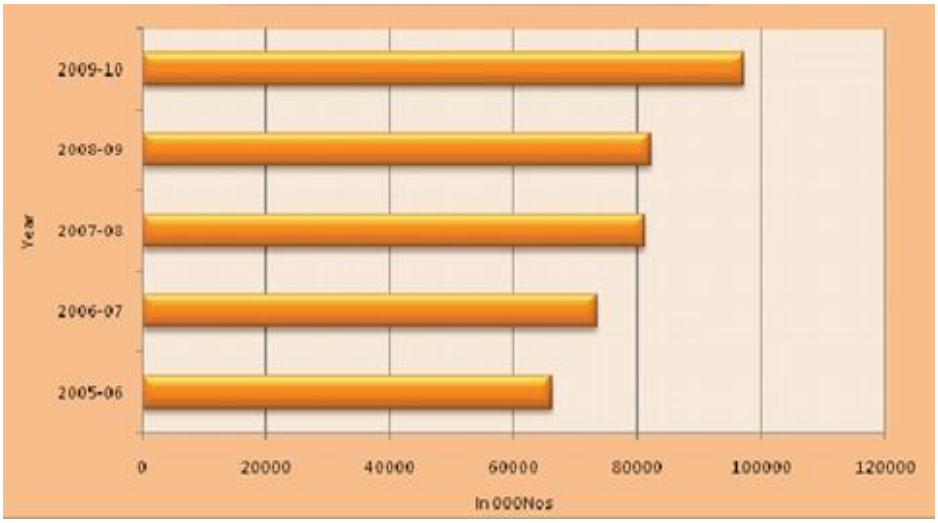


Fig 2.2 Production of tyre in India

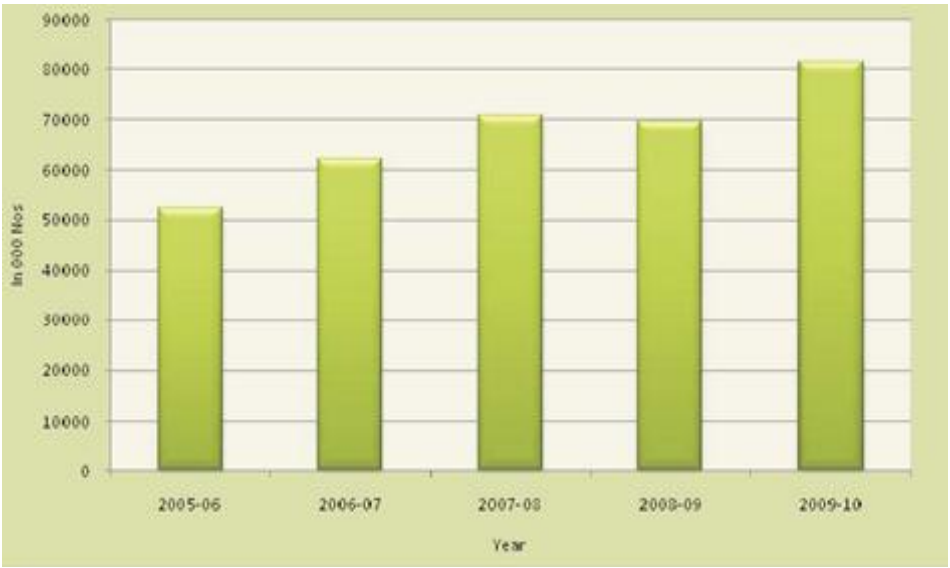


Fig 2.3 Production of tube in India

2.2.1 Natural rubber

The chemical formula of natural rubber is a polymer of isoprene (2-methyl-1, 3 butadiene). Natural rubber is produced from the sap of rubber tree (Heveabrasiliensis) which grows primarily in South East Asian countries; there are a number of other trees that also produce rubber such as the Ficuselastica, which is a native of the Congo, and Guayule, a desert scrub from Mexico and Arizona. Hevea is a native of the Amazon basin and until about 1910 the majority of natural rubber was derived from trees growing wild in this region [11].It can withstand temperature up to the range of 10-60^{o}C, has tensile strength 200 kg/cm^{2} and it has high elasticity ranging from 300 to 1000 % [12,13].

2.2.2 Synthetic rubber

Synthetic rubber is artificial rubber, made from raw materials such as butadiene, styrene, isoprene, chloroprene, isobutylene, acrylonitrile, ethylene and propylene. More than half of the world's synthetic rubber is styrene-butadiene rubber (SBR) made from styrene and butadiene monomers which are abundant in petroleum. Three quarters of all the SBR made goes into tyres. The rest goes into products such as footwear, sponge and foamed products, waterproofed materials, and adhesives. Styrene butadiene rubber resembles natural rubber in processing characteristic as well as finished products. It possesses high abrasion-resistance, high load-bearing capacity and resilience. On the other hand, it gets readily oxidized, especially in presence of traces of ozone present in the atmosphere. Butyl rubber which is used in tyre inner tube, is also a synthetic rubber produced by the polymerization of isobutene with a small amount of isoprene. It is impermeable to air and other gases, that are used in tyre inner tube and other products which require a good barrier against gases. The thermal stability of these rubbers makes them suitable for use in automotive radiator hoses. Their ozone resistance makes them appropriate for electrical insulation and for weather resistance. Their ability to absorb shock is

earning them wide application in automotive suspension bumpers. These rubbers also have a few disadvantages they are incompatible with many natural and synthetic rubbers, they tend to pick up foreign matter and impurities, and they lose elasticity at low temperatures [11, 12, 13].

2.2.3 Reclaimed rubber

Reclaimed rubber is defined as devulcanized rubber that has regained its viscosity as well as the characteristics of the original compound. This reclaimed rubber is made by the treatment of ground vulcanized scrap of rubber tyre, tube and miscellaneous waste rubber articles, through the application of heat and chemical agents. This is followed by intense mechanical working, which gives regenerated rubber almost original plasticity. Devulcanized material (i.e. reclaimed rubber) is also used as raw material for new tyres manufacturing. The reclaimed rubber is of less tensile strength, lower in elasticity and possesses lesser wear-resistance than natural rubber. However, it is much cheaper, uniform in composition and has better ageing properties [11, 12]. Table2.1 shows the consumption of rubber in India (quantity in metric tonnes). The use of natural rubber increased by 23.1%, synthetic rubber by 40.5% and reclaimed rubber by 37.1% from the year 2005 to 2010. Consumption of natural rubber is 442921 metric tonnes in the year 2005-06 which subsequently increases to 576210 metric tonnes in the year of 2009-10. In the same way production of both synthetic rubber and reclaimed rubber has increased from 141580 and 21978 metric tonnes in the year 2005-06 to 576210 and 34986 metric tonnes in 2009-10. The overall consumption of rubber in tyre sector has increased by 32.1% from the year 2005-06 to 2009-10.

Table 2.1: Rubber consumption in India sector wise (Quantity in Metric Tonnes) [1]

Year/Sector/Rubber		2005-06	2006-07	2007-08	2008-09	2009-10
Tyre sector	Natural	442921	462081	495526	508121	576210
	Synthetic	141580	1708091	190987	185094	238153
	Reclaim	21978	23714	27319	29191	34986
Grand Total		606479	656604	713904	722406	894331

Rubber mostly consists of blends of two or three rubber compounds mixed with tyre additives. For example, the tread components can consist of blends of NR and SBR, compounded with carbon black, oils, and vulcanizing chemicals. The sidewall materials consist of a NR/BR blend. The structural formulas of rubber compounds can be distinguished from one another, but the main structures are similar. Polymers are high molecular weight compounds made from multiple low molecular weight building units, or monomers. Polymer structures may consist of 1000-20000 repeating units of single or double bonded carbon-hydrogen monomers. For instance, NR is a polymer composed of isoprene, butadiene, and styrene and isobutyl units. SBR is a combination of styrene, alkane and alkene units [7] as shown in Fig 2.4, Fig 2.5 and Fig 2.6

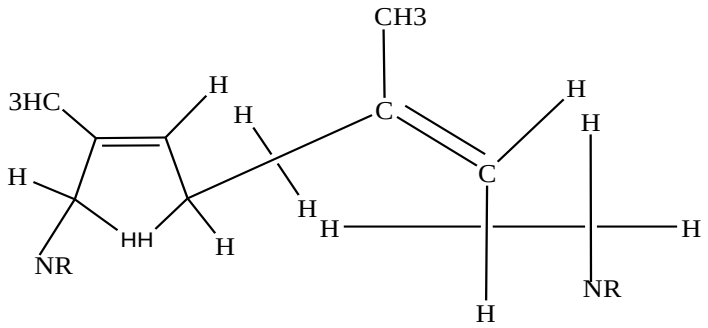


Fig 2.4 Natural Rubber (NR)

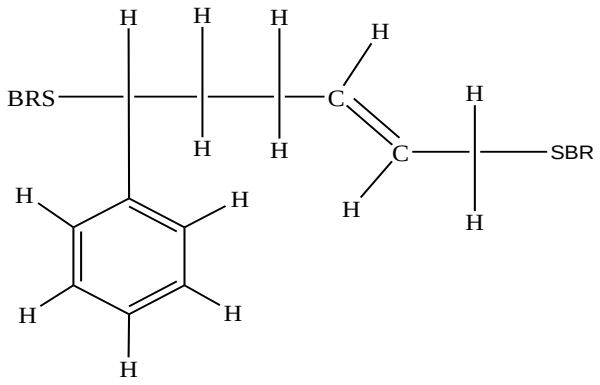


Fig 2.5 Styrene-Butadiene Rubber (SBR)

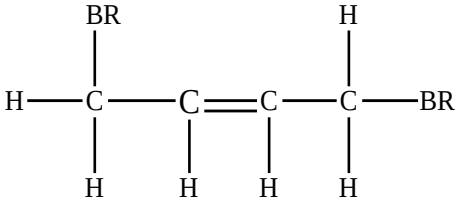


Fig 2.6 Butadiene Rubber (BR)

Structure formula of rubber compounds

2.3 Waste generation of tyre and tube

Tyre and tube are the backbone of the bicycle and rickshaw. Bicycle and rickshaw continue to be the principal mode of transport for the low and middle income families. This is because the bicycle is both environment and people friendly. India is largest producer of bicycle next to only China. The future of the bicycle industry is bright. However, for survival the companies have to successfully restructure and modernize to achieve global competitiveness in terms of quality, cost and distribution system. The tyre and tube industry is a major consumer of the domestic rubber production [10]. There is very good domestic as well as export demand of bicycle and rickshaw tyre and tube. On the other hand cycling is

potentially an important mode of sustainable transport because it is non-polluting, inexpensive, and good for users health and improves the quality of urban life. But the amount of cycling in most cities worldwide remains well below its potential. Bicycle production was up by 3.2% in 2007 to 130 million units, a continuation of the upward trend that has been characterized with the increase in production for most of this decade .India produces approximately 10% of the world annual bicycles [10, 14]. However with increased production of bicycle the production of tyre and tube will also be increased which is proportional to the volume production of wastes.So the generation of solid wastes like tyre and tube is increasing steadily. According to the statistical data with the exponential growth in number of automobiles, generation of waste tyre and tube increases.In 2009, over 400 million scrap tyres were generated and over 3 billion worldwide; which is estimated to be exceeding 1 billion in scrap piles throughout India [3]. So, from the case study by (Hird et al., 2002) it was predicted that there is an urgent need to identify viable recycling routes for waste tyres. As shown in Fig 2.7tyre recycling is predicted to remain flat in the UK up until 2012 with the only growth being in energy recovery. A major use in energy recovery is as a fuel source for cement kilns, where tyres produce 20% more energy than coal. A considerable shortfall in the capacity of the UK to reprocess its used tyres is also predicted due to the lack of economically viable alternatives to landfill [15].About 80% of people living in rural areas use bicycle. There is also restriction of use of car and motor bikes in different places particularly in educational institutes increasing the demand for the use of cycle. This will produce a lot of tyre and tube wastes. Production of these wastes can cause many environmental and hygiene problems. The mass up of this waste in the land filling sites cause problems such as:

- Breeding of insects, mosquitoes etc.
- Emissions of pollutants and obnoxious gases.
- Requirement of more land filling sites
- Water contamination

Thus, researchers have put many efforts in developing different ways of reusing them.

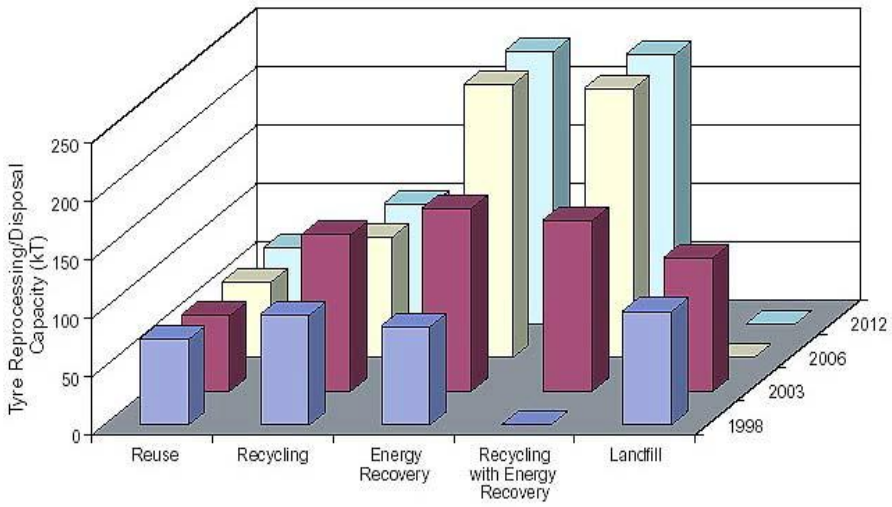


Fig 2.7 Predicted (best case) tyre reprocessing capacities by category (Hird et al., 2002)

2.4 Different types of recycling process to reduce the tyre and tube waste

Pyrolysis, gasification and liquefaction are the thermo-chemical processes that can be used to convert waste tyre and tube as well as other carbonaceous feed stocks such as coal, wood waste, or municipal solid waste into usable products.

2.4.1 Pyrolysis process

Pyrolysis is one of the unique methods of recycling the organic waste. It is a thermo-chemical process which involves heating organic waste material at higher temperatures in the oxygen free atmosphere to break them down to simpler organic compounds. Carbon, solid char, oil and gas are produced on the pyrolysis of organic solid wastes. For example, pyrolysis can convert wood

to charcoal and a low-Btu gas. Pyrolysis usually occurs at temperature between 400°Cand 800°C. In case of pyrolysis, lower temperature produces more oil products and higher temperature produces more gases [16]. This process has a number of advantages. The derived oil from tyre pyrolysis may be used directly as fuels or added to petroleum refinery feed stocks, and also helpful for the refined chemicals. The derived gases are also useful as fuel and the solid char may be used either as activated carbon and carbon black [17, 18]. As studied by *Islam M.R et al.* pyrolysis basically involves the thermal decomposition of the tyre rubber at high temperatures (300-900^{o}C) in an inert atmosphere. The pyrolysis of solid tyre wastes has received increasing attention since the process conditions may be optimized to produce high energy density oils, char and gases. In addition, the oil products can be stored until required or readily transportation to where it can be most efficiently utilized. The tyre pyrolysis oils production pathway with their wide range of potential opportunities for heat, chemicals, fuels and electricity applications are indicated by, Fig 2.8[19].

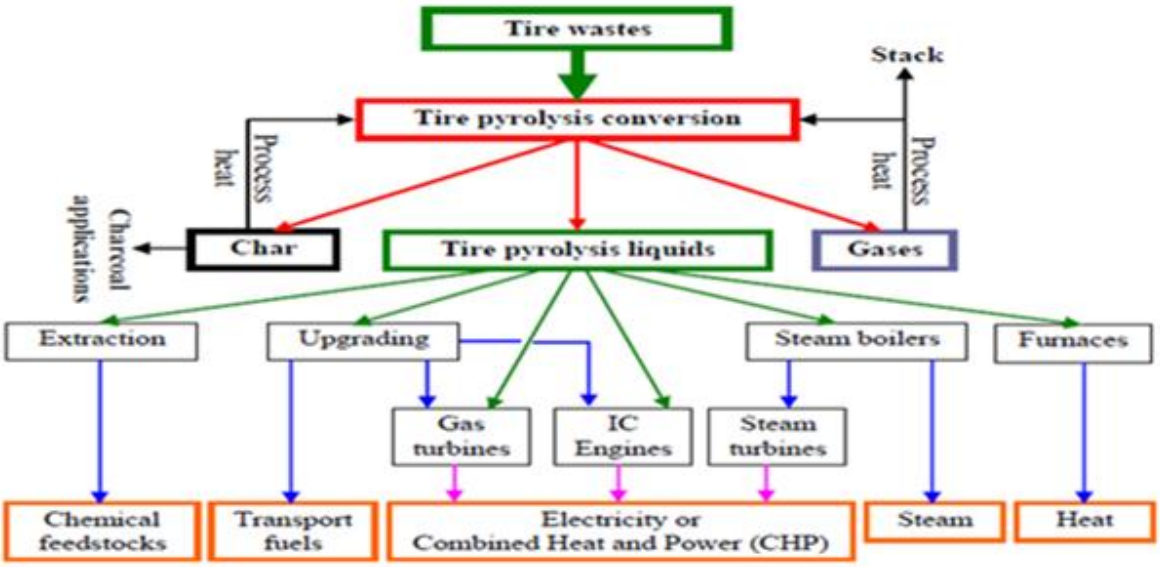


Fig 2.8 Tyre pyrolysis conversion and applications of products [19]

2.4.2 Thermal pyrolysis

Thermal pyrolysis is the decomposition of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 500-900^{o}C and it results in the formation of a carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil and a non-condensable high calorific value gas. Several researches have taken place on production of hydrocarbon oils from waste tyre by thermal pyrolysis. Solid motorcycle tyre waste was thermally pyrolysed in a fixed bed reactor under different operating conditions with different feed size of (2 cm^3, 4 cm^3, 8 cm^3 and12 cm^3). The optimum oil (49%) was obtained at 475^{o}C with feed size of 4cm^3 [20]. The derived tyre pyrolytic oil from thermal pyrolysis of waste tyre under static-bed batch reactor at a different range of 450–600^{o}C was characterized and it was found that the fuel property was similar to light petroleum fuel oil. The temperature has a major influence for increase in the aromatic content of the oils, with a consequent decrease in aliphatic content [18]. *Pakdel H et al.* developed the vacuum pyrolysis process for used tyres and got 45% of oil from which 27% was naphtha and showed that the mass spectrometry provides superior quantitative capabilities, while infrared spectroscopy is an excellent complementary technique for simultaneous qualitative analysis of pyrolytic oil [21].

Kyari et al. considered pyrolysis analysis of seven different brands of used car tyres from several countries throughout the world and characterized the product oils obtained from individual and mixture of seven categories of tyre wastes. They reported that there had been major variation in concentration of different compounds presented in the derived oils and gaseous products[22].During the pyrolysis of car tyre it was observed that there was no significant influence of temperature and characteristics of pyrolysis products over 500^{o}C. The obtained oils are a complex mixture of C_5 - C_{20} organic compounds, with a great proportion of aromatics with

high gross calorific values of 42MJKg^{-1}. The obtained pyrolysis gases composed of hydrocarbons of which C_1 and C_4 are predominant, together with some CO, CO_2 and$SH_2$and they have very high gross calorific values (68–84 MJ Kg^{-1}).On the other hand authors have also demonstrated that at 500^{o}C, 600^{o}C and 700^{o}C and at longer reaction time do not decrease solid yields in tyre pyrolysis. Therefore, it can be concluded that tyre decomposition at 500^{o}C, 600^{o}C and 700^{o}C is complete and that ≈3–4% of char or carbonaceous material is produced [9]. Pyrolysis of waste tyre at different degradation rate and product yields has been studied by *Y.M Chang.* and proved that the effect on the degradation rate of a pyrolysis temperature of below 400^{o}C is more sensitive than that above this temperature. The total yield of gas products is 30-53%, oil yield is28-42%, and char yield is 14-28%by weight. Further, the fuel oil, a part of the oil product, has a maximum level up to 15% by weight at a temperature of 350^{o}C [23]. The recycling of rubber from old tyres by batch hydrogenation has been performed using tubing bomb reactors. Process variables such as temperature, reaction time, initial hydrogen pressure and nature of gas used have been studied and it was shown that, high temperature does not increase rubber conversion but decreases oils yield. A similar trend was found when long reaction times are used. No difference in conversion and yields was found when nitrogen was used. Results are very similar to those obtained when high hydrogen pressures are used concerning to oils quantity but not to oils quality [24].

Experimental and theoretical investigation of combustion and pyrolysis of a single rubber particle was studied by *Zuzana. K et al.* Experiment were carried out by using TGA analyzer and different conditions for particle ignition were investigated, with initial temperature ranging from 500-700^{o}C and initial concentrations of oxygen varying from 5 to 21 mol%. It was shown, that the combustion time depends on pyrolysis conditions. This fact can be due to different pore

structure development inside the particle [25]. Many factors that affect the light oil fraction of oil produced during pyrolysis of waste tyres were investigated with GC-MS, FT-IR, and chromatographic column as separation means. The results showed that carrier gas flow rate, heating rate, and temperature influence the percent of light oil. Compared to N_2 and water vapour as carrier gas, CO_2 can better improve the fraction of light oil and reduce the fraction of heavy oil. Fast flow rate can give greater benefit to increase of the percentage of light oil. In contrast to this, fast heating rate is not favourable to improve the yield of light oil. The depth of pyrolysis was seriously related to the temperature. The content of PAH compounds in the pyrolytic oil always increased under the condition of less than 800^oC as the temperature was raised [26].

Pyrolysis of rubber appears to be a logical choice, all the more because, apart from minor fugitive sources and equipment leaks, this process products virtually no emissions. One of the problems with thermal pyrolysis is that of wide oil product distribution with poor economical value. Therefore, catalytic pyrolysis, an alternative technique to thermal pyrolysis, is under extensive exploration [27].

2.4.3. Catalytic pyrolysis:

The derived oils from tyre pyrolysis without catalyst have been revealed to be highly aromatic, which are partial to be used as an alternate oil fuel. Since the derived oils contain concentrations of valuable chemicals such as benzene, toluene, xylenes, etc., so they can be extracted from the derived oils and used as chemical feed stocks in the chemical industry. So catalysts are used to produce more single ring aromatic compounds during tyre pyrolysis. The waste tyre has been pyrolyzed by using zeolite USY catalyst and studied the influence of the pyrolysis temperature, catalytic temperature, catalyst/ tyre ratio and heating rate on the yield of the products. The results showed that the influence of the presence of zeolite USY catalyst was to reduce the yield of oil with a consequent increase in the gas yield. The yields of oils decreased largely as the catalytic

temperature and catalyst/ tyre ratio increased and the yield of light naphtha (<160^{o}C) distilled from the derived oil was found to be influenced by pyrolysis temperature, catalysis temperature and catalyst/tyre ratio, and was around 60 wt% in the derived oil [28].*Williams and Brindle*[29]used zeolite ZSM-5 and two zeolite Y-type catalysts with different Si/Al ratios and pore sizes to study the influence on the yields of products and the composition of derived oils. The Y-zeolite catalyst had a lower silica/alumina (SiO_2/AlO_2) ratio and therefore higher surface acidity and also possessed a larger pore size than the ZSM-5 catalyst. The Y-zeolite catalyst produced significantly higher concentrations of benzene, toluene, xylenes, and naphthalene and alkylated naphthalene compared to the ZSM-5 catalyst. *OlazarMetal* has used HY and HZSM-5 zeolite catalysts in the pyrolysis of used tyres in a conical spouted bed reactor. The significance of the different shape selectivity of HY and HZSM-5 zeolite is apparent in the transformation reactions of thermal pyrolysis primary products. The capacity of the HZSM-5 zeolite catalyst has major influence for obtaining high yields of olefins (particularly ethene and propene) decreasing the molecular weight of the oil fraction and decreasing the yield of tar compared to thermal pyrolysis. Both catalysts increase the yield of the aromatic fraction (with a high concentration of xylenes) compared to thermal Pyrolysis [30]. The waste tyre represents a source of energy and valuable hydrocarbon products. The effects of basic catalysts (MgO and $CaCO_3$) were studied on the products of waste tyre pyrolysis and results showed that higher amount of oil were obtained with catalytic pyrolysis at 350^{o}C. Fuel properties of oil derived from tyre pyrolysis with MgO and $CaCO_3$ catalysts were comparable with diesel fuel. About 40% of hydrocarbons were present in the oil derived from MgO as catalyst and oil derived by using $CaCO_3$as catalyst has 10% gasoline fraction. The pyrolytic oil from MgO catalytic pyrolysis of waste tyre contained about 55 % aromatic hydrocarbons whereas aromatic fraction in oil from $CaCO_3$ catalytic pyrolysis was 50% [31].Catalytic pyrolysis of waste tyres using two different zeolite catalysts

has been investigated in relation to the influence of the catalyst temperature on the yield and composition of the products. The waste tyres were pyrolysed in a fixed bed reactor and the evolved pyrolysis gases were passed through a secondary fixed bed reactor containing zeolite catalyst. It was observed that the presence of catalyst reduce the yield of oil with a consequent increase in the gas yield and formation of coke on the catalyst. Single ring aromatic hydrocarbons, benzene, toluene and xylenes present in the oils showed a marked increase in the presence of the catalyst. Naphthalene and alkylated naphthalene were also analyzed and showed a similar marked increase in the concentration when a catalyst was present. Increasing the catalyst temperature resulted insignificant changes in the concentration of benzene, toluene, xylenes, and naphthalene [32]. The conversion of waste tyre rubber into valuable oil hydrocarbons was investigated using catalytic pyrolysis. The mixture of an acidic (SiO_2), basic (Al_2O_3) catalyst used for pyrolysis, in which the yield of derived gas, oil and solid has been studied in term of the temperature, time and amount of catalyst. Oil derived with Al_2O_3 containing higher concentration of polar hydrocarbons (40%) and lower concentration of aliphatic hydrocarbons while 40% aliphatic hydrocarbons and 30% polar hydrocarbons were found in oil derived with SiO_2. A mixture of catalyst (Al_2O_3: SiO_2) gave equal concentration of aliphatic (35%) and polar (35%) hydrocarbons in oil [33].Evaluation of waste tyre rubber using catalytic pyrolysis is very important from economical and environmental point of view as the gas and oil can be utilized and since as catalytic pyrolysis using solid bases as catalysts requires lower temperature.

2.4.4 Gasification:

Gasification of organics occurs at operating conditions between the complete absence of oxygen and stoichiometric (i.e., sufficient oxygen to complete the oxidation reaction).Gasification involves drying and paralysing a feedstock, and oxidizing the solid char to heat the reaction and

provide carbon monoxide (CO) to the gas. Gasification is generally carried out at higher temperatures (700-1400^{o}C) than pyrolysis and in the presences of a partially oxidative reactive atmosphere. In the early 1980s, the waste industry saw gasification as promising. Gasification processes maximized the effect of carbon-hydrogen ratios. Furthermore, the product gas was suitable for use in existing boilers [34].Gasification of scrap tyres seems to be an attractive method since the gaseous fuel product can be stored, transported and easily fueled for existing boilers and combustors with little modification. The characteristics of syngas evolution during pyrolysis and gasification of waste rubber have been investigated; Gasification resulted in more than 500% increase in hydrogen yield as compared to pyrolysis at 800^{o}C [35]. One of the disadvantages of the conventional gasification system is the high temperature that is required for decomposition of the feed stock and for the reforming reactions, which affect the overall energy efficiency of the process [36].

2.4.5 Liquefaction:

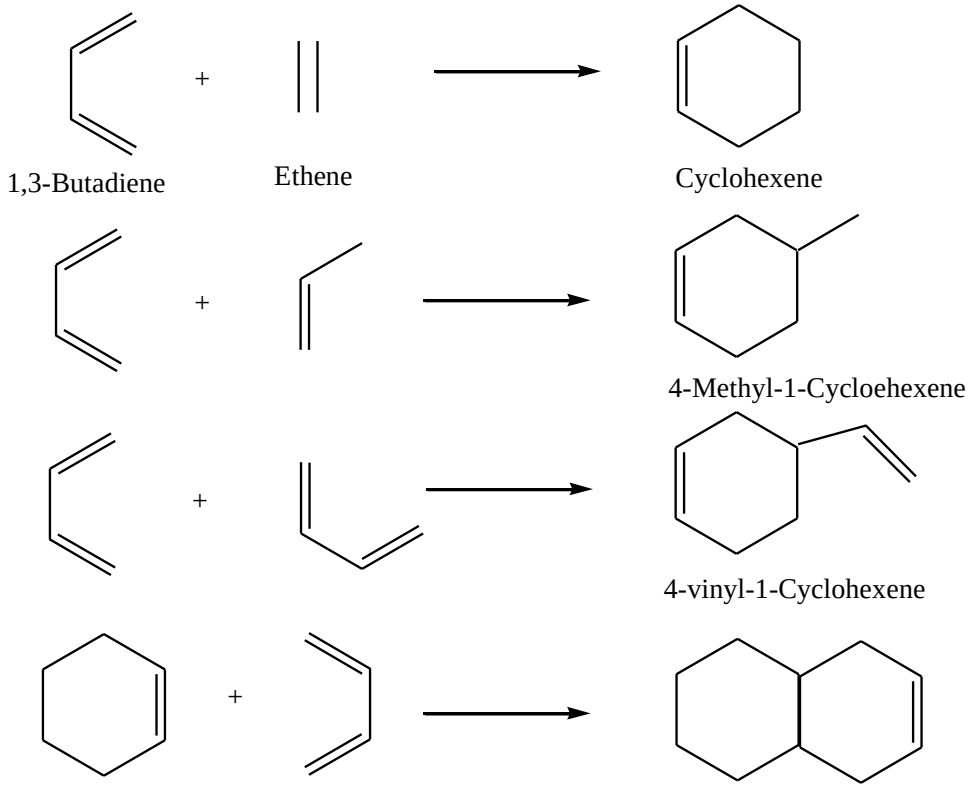
Liquefaction is the thermochemical conversion of an organic solid into petroleum-like oil. Liquefaction typically involves the production of oil composed of heavy molecular compounds from a pyrolytic gas stream. It encourages the production of oil, which can be upgraded to transportation fuels. The oil has properties similar, but not identical, to those of petroleum-based fuels. Essentially, liquefaction is manipulation of the pyrolysis process in order to produce oil with characteristics similar to petroleum-based oils (e.g., fuel oils) [34].Tyres could be liquefied singly, or in combination with other waste materials and/or coal in co-processing schemes, in one or two stage processes. The idea of including tyres into a coal liquefaction process has been proven to be more advantageous on a development plant scale. Liquefaction provides an effective approach for converting the organic content into oils. Pyrolysis offers an alternative approach and is simplified since solvent is not needed.

D.M. Money et al. studied the liquefaction process of scrap automobile tyres by using different solvents and solvent mixes (process derived recycle solvent (PDRS) or tyre pyrolysis oil (TPO) or a mixture of the two solvents). Experiments were carried out at different temperatures (360, 380, 400^{o}C) and for different reaction periods (400^{o}C, 1 or 2 hr).The results have shown that tyre can be depolymerised and dissolved in PDRS, with dissolution of all the organic content under relatively moderate reaction conditions which are similar to those used in coal liquefaction. When. TPO was used as solvent; dissolution was less than PDRS under comparable conditions, especially at 380^{o}C when retrograde reactions occurred due to the low H-donor capacity of the TPO. No significant pressure build up was noted in any of the liquefaction experiments .Liquefaction was found to be a superior process than pyrolysis and hydropyrolysis which minimizes gas formation and maximizes oil yields [37].Work by *Harrison and Ross* [38] showed that the addition of TPO at this level would not be detrimental to coal dissolution and suggest that coal and scrap tyres could be used as a feed to the dissolution stage of two stage coal liquefaction, which could use a recycle solvent augmented by TPO to dissolve the feed, without detriment to the extent of dissolution of the individual components of the feed. Liquefaction could also provide an effective way of dealing with scrap tyres independently, but problems with filtration caused by the presence of carbon black would need attention if excessive filtration times are to be avoided.

2.5 Reaction mechanisms occurred during pyrolysis of tyre:

Pyrolysis of tyre depends on the various parameter and reactor type. Tyre is made up of different type of rubber compounds such as natural rubber (NB), butadiene rubber (BR), or styrene butadiene rubber (SBR)and these rubbers basically consists of different types of polymer. During the pyrolysis of tyre different types of polymerization reactions are formed inside the reactor.

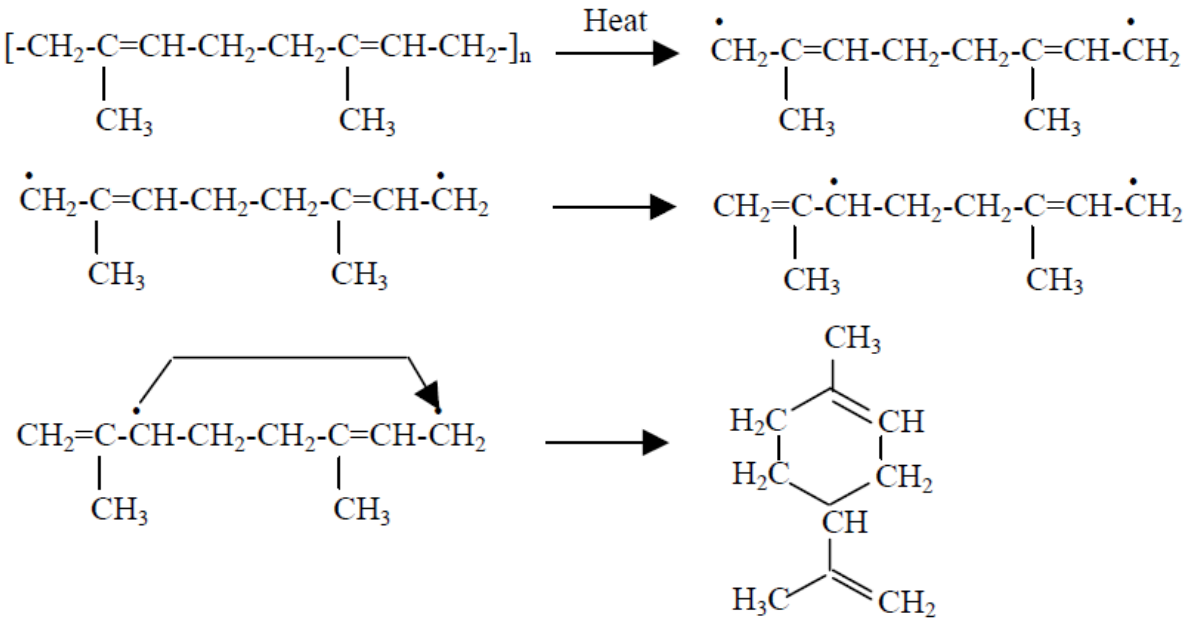
Cypres and Bettens [39] suggest that the pyrolysis of tyres leads to the production of ethene, propene and 1, 3-butadiene, which react to form cyclic olefins. These reactions are given as follows:



Sheme-1 Reaction mechanism during pyrolysis of tyre

Tamura et al. have also shown that isoprene and dipentene are formed in high concentration in natural rubber pyrolysis and have suggested that both are produced by depolymerization from the polymer radicals occurring by β-scission at double bonds. The polymer radicals are liable to form six-membered rings, especially under mild pyrolysis conditions, so the dipentene is formed predominantly at lower temperature [40]. *Bhowmick* also examined pyrolysis of natural rubber using TGA. They showed that degradation started at ~330°C in nitrogen, with a peak weight loss

at ~400°C. They found that decomposition of tyre is by radical generation via polymer chain scission and results in the formation of isoprene, dipentene and other smaller compounds [41].The thermal decomposition mechanism of waste tyre has been described by *M Rofiqul et al* and they found that polyisoprene has depolymerized forming dimeric species. Correspondingly the dimmer species, a short-life radical, could be stabilized through a two-step process driving to limonene by pyrolytic isomerization, as it happens from propylene to cyclopropane according to the following mechanism [42, 43].



Scheme 2 Reaction mechanism during pyrolysis of tyre

CHAPTER 3

3. Experimental

3.1 Materials and methods

The raw materials used for the pyrolysis process was bicycle waste tyre and tube. The Indian made different company based GRL; RALSON has been collected from the nearby bicycle repairing shops, Rourkela, India. Bicycle waste i.e. tyre and tube samples were cut into approximate size of 1 cm. The steel thread was removed from the tyre. Before pyrolysis it has taken for proximate and ultimate analysis and compared with motor cycle tyre which is shown in Table 3.1.

3.1.1 Proximate and ultimate analysis of raw material

The proximate analysis was done by ASTM D3173-75. And the ultimate analysis was done by using Elemental CHNS analyzer. Calorific value of the raw material was found by ASTM D5868-10a.The samples such as tyre and tube were identified with the following characteristics using proximate and ultimate analysis. Table 3.1 gives an idea for thermal degradation of the sample showing more volatile content along with moderate fixed carbon composition. From ultimate analysis bicycle tyre and tube shows less carbon content and more oxygen content when compared with tyre (of motor cycle). Hence the GCV of bicycle tyre and tube were varying a small difference as compared to the motor cycle tyre but in appreciable range to recover when compared with coal [20, 44].

Table 3.1 Proximate and Ultimate analysis of Tyre and Tube

Types of used Raw material	Tyre	Tube	Motorcycle Tyre [20]
Proximate analysis			
Moisture content	0.55	0.63	1.53
volatile matter	62.00	55.00	57.50
Ash content	18.73	26.00	20.85
Fixed carbon (By difference)	18.72	18.37	20.10
Ultimate analysis			
Carbon (C)	57.38	36.61	75.50
Hydrogen (H)	5.50	3.92	6.75
Nitrogen (N)	0.67	0.05	0.81
Sulphur (S)	3.24	1.86	1.44
Oxygen (O)	33.21	57.56	15.50
H/C Molar ratio	0.10	0.11	N/A
C/N Molar ratio	86.26	682.85	N/A
Empirical formula	$C_1H_{1.15}N_{0.01}S_{0.02}O_{0.43}$	$C_1H_{1.28}N_{0.00126}S_{0.02}O_{1.18}$	N/A
GCV (Mj/Kg)	27.68	17.23	29.18

3.1.2 Thermogravimetric Analysis

The TGA analysis of tyre and tube raw material has been characterized by thermogravimetric analyser DTG-60/60Hof SHIMADZU.

3.1.3 Semi-Batch Pyrolysis Reactor

Semi-batch pyrolysis reactor which was made of stainless steel (SS) (length- 16.5cm, 4.7 cm internal diameter and outer diameter- 5.0 cm) sealed at one end and an outlet tube at other end.

3.1.4 Pyrolysis setup

Fig 3.1 shows the schematic representation of pyrolysis set up which consists of a reactor-furnace system in which the furnace temperature was maintained constant using a PID controller. At the outlet of reactor, a condenser was attached to condense the vapours coming out of it. The condensed oil was collected in a collecting jar at the end of condenser.

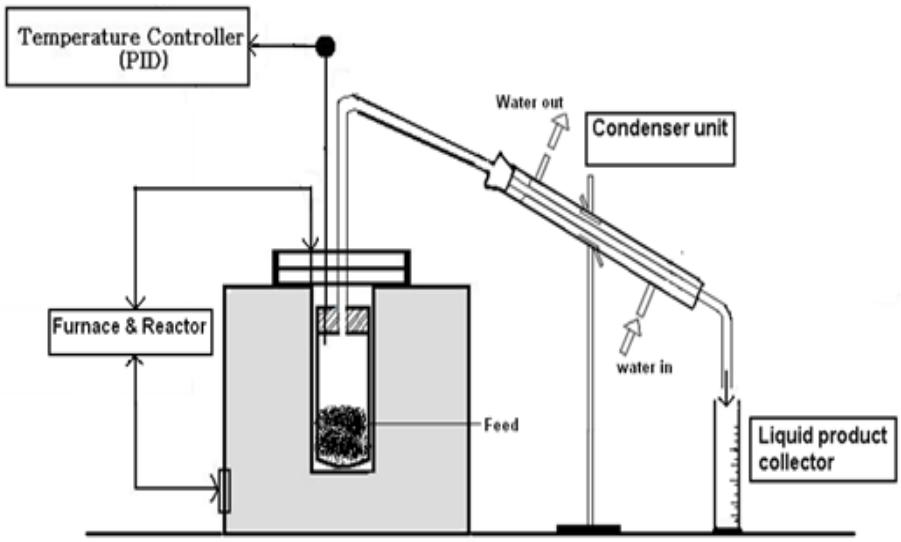


Fig 3.1 Schematic diagram of pyrolysis set up

3.1.5 Experimental Procedure

20gm of waste tyre and tube sample was taken in the stainless steel reactor for each run and placed in an electrically heated furnace. Pyrolysis experiments were carried out in the reactor at various temperature ranges from 450^{o}C to 700^{o}C for tyre and 450^{o}C to 800^{o}C for tube with a heating rate of 20^{o}Cmin^{-1}. The vapour from the reactor was condensed in a water cooled condenser and the non-condensable gas was vented to atmosphere. The condensed oil was collected from the outlet of the condenser in a measuring cylinder, and weighted. The remaining residue collected and weighted after cooling the reactor**.** The weight of non-condensable gases was measured by mass balance.

3.2 Catalyst used

Four types of different catalyst were used in this experiment i,e SiO_2-AlO_2, Kaolin, CaO, and MgO. This catalyst were taken in powder form and activated at 500^{o}C in muffle furnace.

3.3Characterization of pyrolytic oil

3.3.1 Chemical characteristics of tyre and tube oil

3.3.1.1Fourier Transform Infrared spectroscopy (FTIR)

The oil was analyzed using Fourier Transform Infrared spectroscopy (FT-IR).The FTIR spectra were collected in the range of 400-4000 cm^{-1} region with $8cm^{-1}$ resolution. The FTIR imaging is carried out using Perkin Elmer RX.

3.3.1.2 GC-MS analysis

The composition of oil derived from tyre and tube pyrolysis was analyzed using gas chromatography/mass spectrometry (GC/MS- QP 2010 SHIMADZU), equipped with flame ionization and mass spectrometry detection (GC-FID-MS). A capillary column coated with a 0.25 um film of DB-5 with length of 30m and diameter 0.25mm was used. The GS was equipped with a split injector at $200^{o}C$ with a split ratio of 1:10. Helium gas of 99.95% purity was used as carrier gas at flow rate of 1.51 ml/min. The oven initial temperature was set to $70^{o}C$ for 2 min and then increased to $300^{o}C$ at a rate of $10^{o}C$/min for 7 min. All the compounds were identified by means of the NIST library. Mass spectrometer was operated at an interface temperature of $240^{o}C$ with ion source temperature of $200^{o}C$ of range 40-1000 m/z.

3.3.2 Physical characteristics of tyre and tube oil

Physical properties such as specific gravity, density, Kinematic viscosity, conradson carbon residue, flash point, fire point, pour point, cloud point, calorific value, sulphur content, distillation boiling range and cetane index of the tyre and tube oil was determined using the following standard methods, which is shown in the Table 3.2

Table-3.2Standard Methods for Physical Property Analysis

Physical Property	Method
Specific gravity	I.S:1448 P:16
Density	I.S:1448 P:16
Kinematic viscosity	I.S:1448 P:25
Conradson carbon Residue	I.S:1448 P:122
Flash point by Abel Method	I.S:1448 P:20
Fire point	I.S:1448 P:20
Cloud Point	I.S:1448 P:10
Pour point	IS:1448 P:10
Gross Calorific Value	IS:1448 P:6
Sulphur Content	IS:1448 P:33
Cetane Index	IS:1448 P:9
Distillation Boiling Range	IS:1448 P:18

3.4 Characterization of pyrolytic char

3.4.1 Proximate and ultimate analysis of the pyrolytic char

The proximate analysis was done by ASTM D3173-75. And the ultimate analysis was done by using Elemental CHNS analyzer. Calorific value of the raw material was found by ASTM D5868-10a.

3.4.2SEM Analysis

The char product derived from the tyre and tube pyrolysis was characterized by Scanning Electron Microscope (Model: JEOL-JSM-6480LV SEM) at different magnification values to have a clear view on pore density and diameter.

CHAPTER 4

4. Results and Discussion

4.1 Thermogravimetry study

Thermogravimetry analysis is performed to know the change in weight with respect to change in temperature. In the present work, TGA was carried out in a Thermogravimetric analyzer (DTG-60/60H – SHIMADZU) in air medium at heating rates of 20°C/min and about the sample size of 15-30mg were applied. The weight loss data was recorded as function of time and temperature.

4.1.1 Decomposition of tyre and tube

Fig 4.1 (a) and Fig 4.1 (b) display the variations of weight loss (TGA curve) and derivative of mass-change (DTG curves) with respect to reaction temperature T at a heating rate of 20°C/min for both tyre and tube samples. In case of tyre two decomposition stages were observed over a temperature range of 33°C to 750°C and three decomposition stages were observed for the tube at a temperature range of 33°C to 800°C. Based on the evaporating characteristics of rubber components, it was assumed that the first decomposition curves were obtained at the temperature range of 33°C to 345°C for tyre and 33°C to 356°C for tube, this was due to the loss of oils, plasticizers and additives present in the tyre and tube. Correspondingly the 2^{nd} stage decomposition of tyre and tube treated as active pyrolytic zone from 345°Cto 550°C and 356°C to 429°C temperature, which also includes the continuous cracking and rapid decomposition of the other tyre components such as NR, SBR and BR as reported by [5]. During the 2^{nd} stage, the intermolecular associations and weaker chemical bonds are destroyed. The side aliphatic chains may be broken and some small gaseous molecules are produced. As a result, the larger molecule decomposes to smaller molecules in the form of gas phase. The particle contains only fixed carbon and constant weight of ash content after 550°C in case of tyre. But in case of tube, the

third stage of decomposition also occurs at a temperature range of 429°C to 733°C due to the secondary depolymerisation of rubber. Above this temperature, sample reduces to ash shown by a constant weight around 800°C. From DTG curves, which explains the dominant peak over 325°C to 455°C for tyre and 317°C to 437°C for tube where more conversion takes place and temperature from 555°C to 687°C and to 687°C to759°C showing two smaller peaks signifying little conversion of butadiene rubber. This agrees with the results of *Williams and Besler* in their [17, 45] thermogravimetric study with two distinct areas of weight loss representing a lower and higher temperature of decomposition.

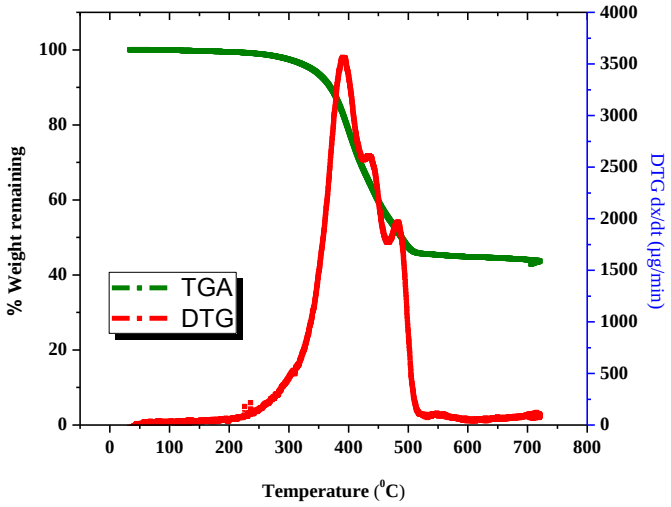


Fig 4.1(a) TGA and DTG curve of tyre

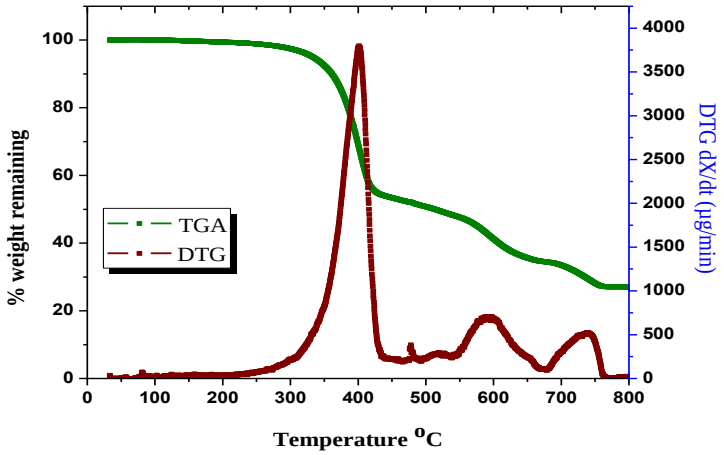


Fig 4.1 (b) TGA and DTG curve of tube

4.2 Thermal pyrolysis of tyre and tube pyrolysis

4.2.1. Effect of temperature on product yield and reaction time of tyre pyrolysis

The product distribution obtained from tyre for temperature range of 450°C to 700°C at every 50°C elevation in temperature for an average feed size as 1cm has been shown in Table 4.1.The reaction temperature, weight fractions of oil, char and volatile along with reaction time were plotted together in the Fig 4.2.It was apparent that at lower temperatures the tyre was partially pyrolysed to give less oil and volatiles with maximum retention of material in solid form as char. With increase in temperature, more gaseous streams were observed at 500°C to 550°C along with moderately high oil products, which increases up to 600°C and that explains the effect of temperature on product yield. It was also proved that oil yield increases from 24.64% to 49.6 % by weight at 450°C to 600°C, there after no significant change occurs. It can be postulated that the optimum yield of oil was obtained at 600°C temperature, due to the strong cracking of tyre rubber and the secondary cracking which takes place inside the reactor, and that was followed by formation of more gases, with a significant decrease in residue from 68.5 % to 41.65% by weight for temperature increase from 450°C to 700°C.With increase in reaction time, results that incomplete depolymerisation of the sample that leads to production of more char and less amount of oil at low temperature. The decrease in reaction times contributes to secondary reaction of the products with higher temperature, which leads to more oil and less char. There is no obvious mechanism for gas loss with reaction time.

Table 4.1Product distribution of tyre pyrolysis

Temperature (°C)	% Oil	% Char	% Gas	Reaction time (min)
450	24.64	68.5	6.85	60
500	39.8	49.9	10.3	52
550	44.55	44.2	11.25	43
600	49.6	42.1	8.3	39
650	49.5	42.05	8.45	35
700	48.75	41.65	9.6	30

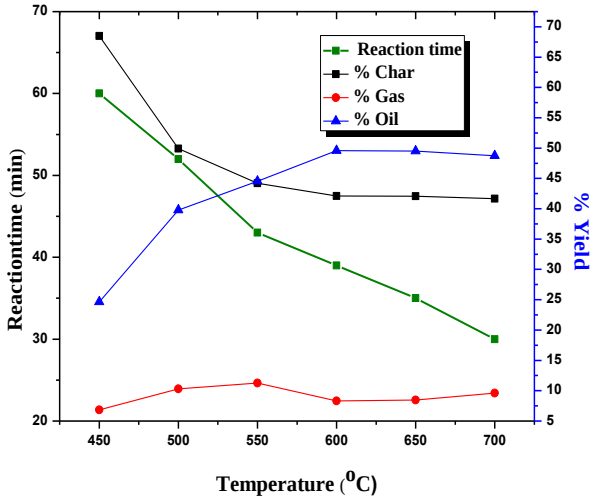


Fig 4.2 Effect of temperature on product yield and reaction time of tyre pyrolysis

4.2.3 Effect of temperature on product yield and reaction time of tube pyrolysis

Similarly, in case of thermal pyrolysis of tube three different products were obtained, which are oil, char and gas. The production distribution yield, reaction time and temperature were presented in Fig 4.3. This shows that the optimum yield of oil was obtained at 700°C by 49.65%.This is probably due to strong cracking at this temperature. The percentage yield of oil

increased from 27% to 49.65% by weight in 450 to 700°C temperature range. At the same time the formation of residue was also decreased from 64.4% to 40% by weight from 450 to 800°C. At higher temperature pyrolysis the secondary cracking takes place inside the reactor, resulting in the formation of more gases. So 700°C was the optimum temperature to get maximum oil from waste tube with a minimum completion time. It was observed that at low temperature with longer reaction time contributes to secondary reaction of primary products, which leads to less oil and more char products. Very short reaction times results in complete depolymerization of the feedstock which leads to more oil and less amount of char with increasing in temperature. Therefore it was suggested that there was a strong effect of temperature on product yields and reaction time. The detail product distribution of pyrolysis of tube compiled in Table 4.2

Table 4.2 Product distribution of Tube pyrolysis

Temperature (°C)	% Oil	% Char	% Gas	Reaction time in (min)
450	27	64.4	8.6	65
500	32	58.85	9.15	50
550	36.5	49.75	13.75	42
600	39.75	48.9	11.35	34
650	49.6	42.25	8.15	35
700	49.65	40.6	9.75	33
750	49.5	40.1	10.4	30
800	49.35	40	10.65	29

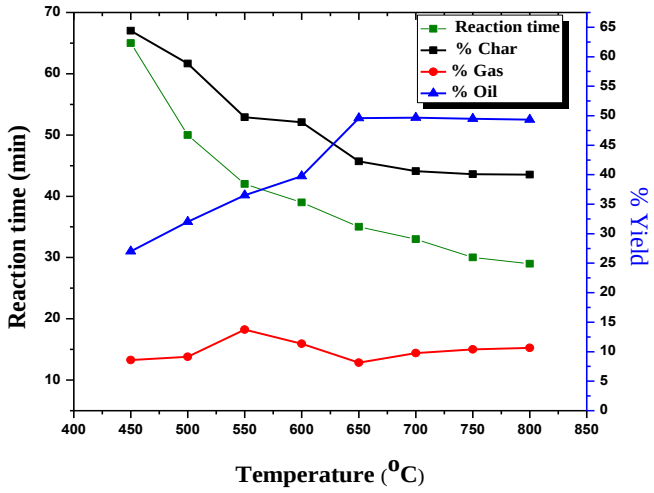


Fig 4.3 Effect of temperature on product yields and reaction time of tube pyrolysis

4.3 Catalytic pyrolysis of tyre and tube

Catalyst is generally used to improve the product yield and to speed up the reaction with minimum temperature. In case of thermal pyrolysis of tyre, the optimum oil yield obtained at higher temperature such as 600°C, and for tube at 700°C. Objective of the study was to increase the yield of oil product. Therefore, some catalysts were used to increase the oil yield with minimum temperature range. So in this study SiO_2-AlO_2Kaolin, CaO, and MgO were used as catalyst for catalytic pyrolysis process with different ratio of (catalyst: tyre) and (catalyst: tube) such as (1:2, 1:3and 1:5). It was observed that catalytic pyrolysis showing no significant effect in comparison to thermal pyrolysis. In future, different catalyst can be used to maximize the oil product yield.

4.4 Characterization of pyrolytic oils

4.4.1Physical properties of pyrolytic oil

The oil obtained after thermal pyrolysis of bicycle tyre and tube waste appears dark brown in colour with strong acidic smell resembling petroleum fractions. The oils were characterized in terms of both fuel properties and chemical composition. The fuel properties of both tyre and tube pyrolytic oil were analyzed by IS-1448 method and compared with diesel and gasoline that has been summarized in Table 4.3

Table 4.3, illustrates that the density of the tyre and tube pyrolytic oil was higher than that of diesel and gasoline. This is attributed to the presence of heavier compounds in the both the pyrolysis oil. The kinematic viscosity of tube pyrolytic oil is nearly same to the diesel. According to *Islam M.R et al*. low viscosity shows the positive quality in the handling and transporting of the oil [18, 20].Conradson Carbon residue was found to be greater than that of diesel. Flash point of a liquid fuel is the temperature at which the liquid begins to evolve vapours in sufficient quantity to form flammable mixture with air. Here the flash point obtained of tyre and tube pyrolytic oils were less than that of diesel and gasoline. The lower flash points of both pyrolytic oils were not surprising since the product obtained is unrefined and contains a mixture of different compounds. Gross calorific values of both the pyrolytic oil were less than that of diesel and gasoline. Sulphur content of both pyrolytic oil was approximately similar to diesel but slightly less than that of gasoline. Cetane Index is a mathematical estimation of the cetane number based on distillation temperatures and density. A cetane Index was specified for automotive or petroleum diesel rather than a cetane number because stakeholder feedback indicated that cetane number could not be easily measured. The calculated cetane indices for both the pyrolytic oils were less than that of diesel. And the distillation boiling point range is nearly similar to diesel but more than that of gasoline.

The important requirement for diesel fuel is its ignition quality, viscosity, and water, sediment, and sulfur contents. Therefore, the pyrolytic oils were requiring preliminary treatments such as decanting, centrifugation, filtration, desulphurization, and hydrotreating to be used as fuels. The treated pyrolytic oil could be used directly as fuel oils or blended with diesel fuels, which will reduce the viscosity and, increase the pH value and flash point of the resulting blends. Consequently, the atomization will be improved, ensuring a complete burnout of the fuel [18]. Based on its fuel properties, tyre-derived pyrolytic oil may be considered as a valuable component for use with automotive diesel fuels. Moreover, the oils may be directly used as fuels for industrial furnaces, power plants, and boilers [17].

Table 4.3 Physical properties of tyre and tube pyrolytic oil

Properties	Tyre oil	Tube oil	Gasoline	Diesel
Density (Kg/m^3)	917.9	918.4	700 to 800	820 to 860
Kinematic Viscosity in @100^0CcSt	5.31	2.94	N/A	2 to 4.5
Conradson carbon residue (%)	0.56	0.90	N/A	0.30
Flash point^{0}C	-9	-10	-43	≥55
Fire point ^{0}C	-4^{0}C	-6^{0}C	N/A	65
Pour point ^{0}C	-87	Below-48	-40	-40 to -1
Cloud point ^{0}C	-12	Below -10	N/A	- 40
Gross Calorific Value (MJ/Kg)	34.61	34.51	47.3	44.00 to 46.00
Sulphur Content (%)	1.38	1.01	3.5	1.2
Calculated CetaneIndex	28	32		50
		Distillation		
Initial Boiling point (^{0}C)	72	72	26.67	172
10 % Recovery	84	82	N/A	194
20 % Recovery	94	162	N/A	209
30 % Recovery	156	180	N/A	226
40 % Recovery	196	208	N/A	243
50 % Recovery	250	252	N/A	260
60 % Recovery	270	278	N/A	277
70 % Recovery	324	328	N/A	296
80 % Recovery	350	340	N/A	316
90 % Recovery	360	N/A	N/A	341
Final Boiling Point	362	360	225	N/A
Residue	6.0 ml	10.0 ml	N/A	N/A
Loss (%)	1.0	2.0	N/A	N/A

4.4.2Chemical properties of the pyrolytic oil

4.4.2.1CHNS analysis of tyre and tube Pyrolytic oil

Table 4.4 shows the elemental composition of both tyre and tube pyrolytic oil and compared with diesel. From the analysis it can be observed that the carbon percentage of both tyre and tube pyrolytic oil is less than that of diesel oil. And the average chemical composition of the both pyrolytic oil has been analyzed as $CH_{1.32}N_{0.01}S_{0.02}O_{0.42}$ and $CH_{1.32}N_{0.0042}S_{0.01}O_{0.13}$.

Table 4.4CHNS analysis of tyre and tube Pyrolytic oil

Element	Tyre oil	Tube oil	Diesel
C	57.79	76.32	85.72
H	6.35	8.37	13.2
N	0.68	0.37	0.18
S	3.01	1.53	0.3
O	32.16	13.40	0.6
Empherical formula	$CH_{1.32}N_{0.01}S_{0.02}O_{0.42}$	$CH_{1.32}N_{0.0042}S_{0.01}O_{0.13}$	$CH_{1.847}N_{0.0017}S_{0.0013}O_{0.00524}$

4.4.2.2 FT-IR analysis of tyre and tube pyrolytic oil

Fourier Transform Infrared (FT-IR) Spectroscopy is one of the important techniques which base its functionality on the principle that almost all molecules absorb infrared light. Only the monatomic (He, Ne, Ar, etc) and homopolar diatomic (H_2, N_2, O_2, etc) molecules do not absorb infrared light. On interaction of an infrared light with oil, chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range regardless structure of the rest of the molecules. Based on this principle functional group present in the pyrolytic oils were identified. The FT-IR spectrum for both the pyrolytic oils is shown in Fig 4.4 and 4.5and results from the transmittance spectrums are presented in Table 4.5 and Table 4.6. The data shows that the present oils contain mainly aliphatic and aromatic compounds.

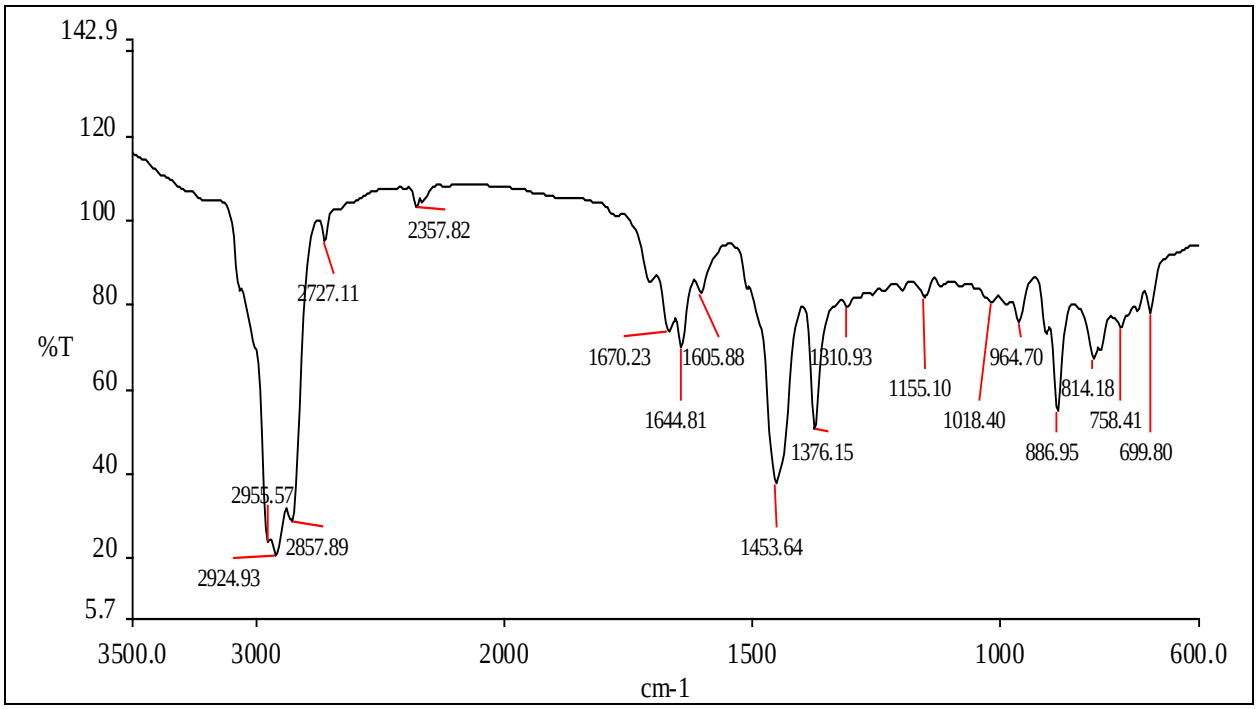


Fig4.4FT-IR spectra of tyre pyrolytic oil

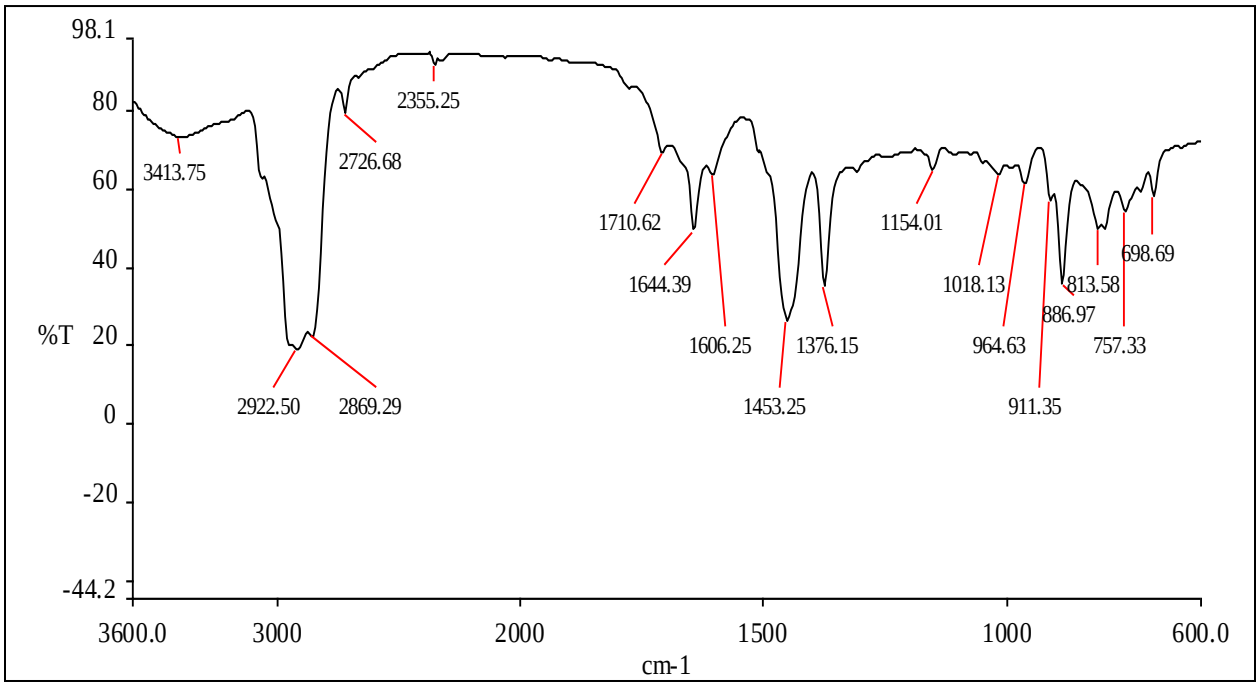


Fig4.5 FT-IR spectra of tube pyrolytic oil

Table 4.5 FT-IR functional groups of tyre pyrolytic oil

Wavelength Range (Cm^{-1})	Functional group	Class of compounds
2955.67	C-H stretching	Alkene
2727.11	C-H stretching	Aldehyde
1670.23	C=Stretching	Aldehyde or ketones
1644.81	C=C stretching	Alkane+ N-H Bend
1605.88	C-C stretching	Aromatic compounds
1453.64	C-H bending	Alkane
1376.15	C-H bending	Alkane
1310.93	C-N stretching	Amines
964.70	C-H bending	Alkene
886.95	C-H bending	Alkene
814.18	C-H bending	Alkene+ Phenyl ring substitution

Table 4.6 FT-IR functional groups of tube pyrolytic oil

Wavelength Range (Cm^{-1})	Functional group	Class of compounds
2726.68-2922.05	C-H stretching	Alkanes, Alkenes, Aldehyde
1710.62	C=Ostretching	Aldehyde or Ketones
1606.25-1644.39	N-H bending=C stretching	Alkene
964.63	C-H bending	Alkene
911.35	C-H bending	Alkene
886.97	C-H bending	Alkene
813.68	C-H bending	Alkane
698.69-799.59	C-H bending	Alkene+ Phenyl ring substitution

4.4.2.3 GC-MS Analysis of tyre and tube pyrolytic oil

GC-MS is one of the modern analytical techniques to identify the possible compound present in the pyrolytic oil derived from different types of organic solid wastes. The oil composition was analyzed in detail for polycyclic aromatic hydrocarbons by chromatography to separate the oils into chemical class fractions followed by gas chromatography/mass spectrometry and gas chromatography/flame ionization detection. Analysis using gas Chromatography/mass spectrometry confirmed the composition of each fraction. GC-MS analyses were carried out for the pyrolytic oils which were obtained at temperature of 600°C for tyre and at 700°C for tube. The NIST software was used to analyze the peaks provided by the chromatogram, from which more than half was not properly identified.Table-4.7, 4.8shows the compounds present and their

percentage area compared to the total area of chromatogram, which gives an estimate for their relative concentration in the pyrolytic oils. It can be seen that both tyre and tube pyrolytic oils are a very complex mixture, containing many aliphatic and aromatic compounds. Such as alkylated benzenes, alkanes, alkenes, tetra methylbenzene, methyl indene, butene and limonene. And it was observed that thirty compounds were obtained in both the pyrolytic oils. The maximum percentage of 4-Isopropenyl-1-Methyl-1-Cyclohexenewas present as compared to other compounds. Similarly in case of tyre pyrolytic oil it contains 39.54 % and 42.17 % in tube pyrolytic oil. D-Limonene is a valuable compound which was found as 2.40% in tyre pyrolytic oil and 3.68% in tube pyrolytic oil. From the different research work it has been proved that, limonene has extremely fast growing and wide industrial applications including formulation of industrial solvents, resins, and adhesives, dispersing agent for pigments, fragrance in cleaning products and as environmentally acceptable solvent [18, 46, 47]. It is very common in cosmetic products and also used as flaming combustible oil. Furthermore, the biological activity of limonene, such as its chemo preventive activity against rat mammary cancer has been recently investigated [18].*Rodriguez et al*. reported that tyre pyrolytic oil produced in a fixed-bed reactor at 500°C consisted of 62.4 wt % aromatic compounds, 31.6 wt % aliphatic compounds, 4.2 wt % nitrogen-containing compounds, and 1.8 wt % sulfur-containing compounds [9].According to *M. Rofiqul et al*. pyrolytic oils are a very complex mixture containing many aliphatic and aromatic compounds with their total concentration of 49.54% and 16.65% respectively [20]. As a summary of the results, it can be concluded that both the pyrolytic oils are a very complex mixture of organic compounds of C_6-C_{17} andC_8-C_{17} carbons and with a very great proportion of aromatics compound. The high proportion of aromatics in tyre oils is attributed to recombination reactions that take place among aliphatic and aromatic free radicals and also to cyclization of

aliphatic chains. This is in accordance with what has been obtained by some other authors [18] which also reports that tyre oils are strongly aromatics.

Table 4.7 GC-MS analysis of tyre pyrolytic oil

R.Time	Area %	Name	Formula
2.853	7.30	1,2-Dimethylbenzene	C_8H_{10}
3.995	2.40	D-Limonene	$C_{10}H_{16}$
4.061	4.03	m-Ethylmethyl benzene	C_9H_{12}
4.376	3.50	(4E,6Z)-2,6-Dimethyl-2,4,6 Octatriene	$C_{10}H_{16}$
4.461	1.22	(6Z)-2,6-Dimethyl-1,6 Octadiene	$C_{10}H_{18}$
4.529	2.25	1,2,3 Trimethyl benzene	C_9H_{12}
4.599	1.75	2,6 Octadiene -2,6-Dimethyl(E)	$C_{10}H_{18}$
4.812	1.44	Trycyclo[5.2.1.0 1,5] Decane	$C_{10}H17$
4.974	8.17	1,4- Diethyl benzene	$C_{10}H_{14}$
5.058	39.54	4-Isoproponyl-1-Metyl-1-cyclohexene	$C_{10}H_{16}$
5.987	3.46	Benzene,Methyl(1 -Methylene)	$C_{10}H_{12}$
6.94	0.97	Benzene,(1 -Methylene-2-cyclopropen-1-yl)	$C_{10}H_{10}$
7.028	0.61	3-Methyllindene	$C_{10}H_{10}$
7.366	0.65	1-Methyl-3-(1-,ethyl-2-propenyl)benzene	$C_{11}H_{14}$
7.668	0.88	1-Methyl-4-(1-,methyl-2-propenyl)benzene	$C_{13}H_{18}$
8.008	0.85	2-Butene, 3-methyl-1-phenyl	$C_{11}H_{14}$
8.459	2.03	2H-Azepine-2-one, hexahydro	$C_6H_{11}NO$
8.502	1.53	1,3 Dimethyl-1H-indene	$C_{11}H_{14}$
10.19	2.10	1,2,3-Trimethyllindene	$C_{12}H_{14}$
10.854	2.32	Pentobarbital	$C_{11}H_{18}N_2O_3$
11.345	4.07	1-methyl-4-(1,5 dimethyl-4-hexenylidene)-1-cyclohexene	$C_{15}H_{24}$
12.001	1.18	(+)-(Z) Longipinane	$C_{15}H_{26}$
12.223	1.74	Napthalene, 2,3,5 Trimethyl	$C_{13}H_{14}$
14.088	0.92	Heptadecane	$C_{17}H_{36}$
14.434	0.63	1,4 dimethyl-7-ethylazulene	$C_{14}H_{16}$
16.239	1.06	Hexadecanitrile	$C_{16}H_{31}N$
16.478	0.99	1-,ethyl-2,4-bis(1- methylethylidene)-1-vinylcyclohexane	
18.226	1.21	Heptadeanenitrile	$C_{17}H_{33}N$

Table 4.8 GC-MS analysis of tube pyrolytic oil

R.Time	Area %	Name	Formula
2.846	10.59	1,2-Dimethylbenzene	C_8H_{10}
3.997	3.68	D-Limonene	$C_{10}H_{16}$
4.062	4.17	m-Ethylmethylbenzene	C_{9H12}
4.374	3.29	(4E,6Z)-2,6-Dimethyl-2,4,6-octatriene	$C_{10}H_{16}$
4.528	3.05	1,2,3-Trimethylbenzene	C_9H_{12}
4.980	8.95	2-Ethyl-1,4-dimethyl-Benzene	$C1_0H_{14}$
5.064	42.17	4-Isopropenyl-1-Methyl-1-Cyclohexene	$C_{10}H_{16}$
5.990	3.51	1-Methyl-4-(1-Methylethenyl)Benzene)	$C1_0H1_2$
6.307	0.34	1-Sce-butyl-4-methylbenzene	$C_{11}H_{16}$
6.479	0.79	1,2,3,5-Tetramethylbenzene	$C_{10}H_{14}$
6.941	1.11	(1-Methyl-2-Cyclopropen-1-yl)Benzene	$C_{10}H_{10}$
7.030	0.59	2-Methylindene	$C_{10}H_{10}$
7.513	0.88	(3-Methyl-2-Butenyl)Benzene	$C_{11}H_{14}$
8.508	1.12	1,3-Dimethyl-1H-indene	$C_{11}H_{14}$
8.598	0.98	1,3-Dimethyl-1H-indene	$C_{11}H_{14}$
10.193	1.76	1,2,3-Trimethyl-1H-Indene	$C_{12}H_{14}$
10.859	1.36	1,5-Dimethylnaphthalene	$C_{12}H_{12}$
11.394	2.25	1-Methyl-4-(1,5-Dimethyl-4-Hexenylidene)-1-Cyclohexene	$C_{15}H_{24}$
12.226	1.46	1,6,7-Trimethylnaphthalene	$C_{13}H_{14}$
12.856	0.45	Hexahydroaplotaxene	$C_{17}H_{34}$
12.902	0.31	Benzene,1-(1,5-Dimethyl-4-Hexenyl)-4-Methyl	$C_{15}H_{22}$
12.944	0.36	Hexadecane	$C_{16}H_{34}$
14.090	0.66	Heptadecane	$C_{17}H_{36}$
14.437	0.41	1,4-Dimethyl-7-ethylazulene	$C_{14}H_{16}$
16.478	1.22	2-Isopropenyl-1-methyl-4-(1-methylethylidene)-1-Vinylcyclohexane	$C_{15}H_{24}$

4.5 Characterization of pyrolytic char

4.5.1 Proximate and Ultimate analysis of tyre and tube char

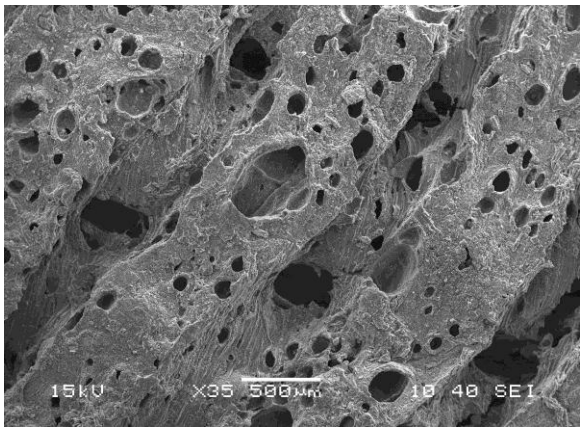
The proximate and ultimate analysis of tyre and tube char has been summarized in Table 4.9.Proximate analysis was used to determine the moisture, ash, volatile, and fixed carbon content and the ultimate analysis was used to determine the elemental composition in terms of carbon, hydrogen, sulfur, nitrogen, and oxygen. The amount of fixed carbon and volatile matter directly affects the heating value. The fixed carbon comprises of carbon black used in tyre and tube manufacture and the volatile matter mainly consists of the polymeric materials. Ultimate analysis showed that the carbon content is more and fewer amounts of hydrogen, nitrogen and sulphur content was present.

Table 4.9 Proximate and Ultimate analysis of tyre and tube char

Material	Tyre char	Tube char
Proximate analysis		
Moisture content	1.12	0.98
volatile matter	4.90	10.60
Ash content	49	65
Fixed carbon	44.98	23.42
Ultimate analysis		
C	87.59	90.01
H	4.61	4.48
N	6.24	5.29
S	1.56	0.22
H/C Molar ratio	0.05	0.11
Empherical formula	$C_1H_{0.63}N_{0.06}S_{0.01}O_{0.000051}$	$C\ H_{0.60}\ N_{0.05}\ S_{\ 0.0009}\ O_{0.000417}$
GCV (MJ/Kg)	39.06	41.20

4.5.2 SEM analysis of tyre and tube char

Scanning electron microscopy is one of the important methodologies to investigate the surface morphology of activated carbon. SEM provides a quick and useful check of the adhesion of such coatings to the substrates. The samples were analyzed first using SEM to determine the appearance of the residue on a microscopic level. The tyre char obtained at 600ºC was taken for study of surface morphology, with different magnifications (35X, 150X, and 200X) are shown in Fig 4.6 (a), 4.6 (b), and 4.6 (c) .The figure shows the heterogeneous distribution of pore and rough texture on surface. From figure 4.6 (d) it was observed that the pore diameter ranges from 31.6µm to 211µm at 100X magnification. Similarly figure 4. 7(a), 4. 7(b) and 4.7(c), shows the SEM images of tube char obtained at 700ºC. The image was taken at a different magnification of (35X, 150X, and 200X).Surface morphology shows heterogeneous distribution of pores and rough texture on surface and has pore size within the range of minimum of 27µm to maximum 90.5µm obtained at 200X magnification is shown in figure 4.7 (d).



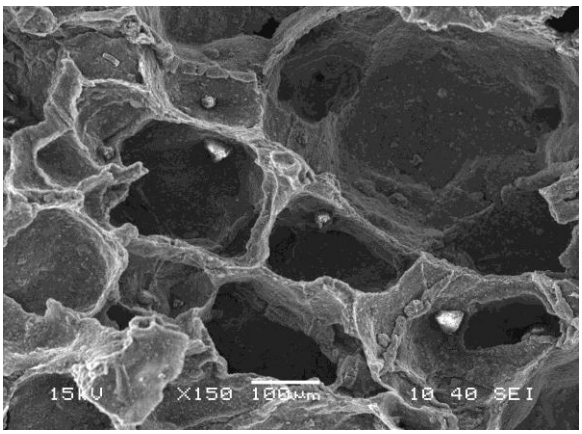
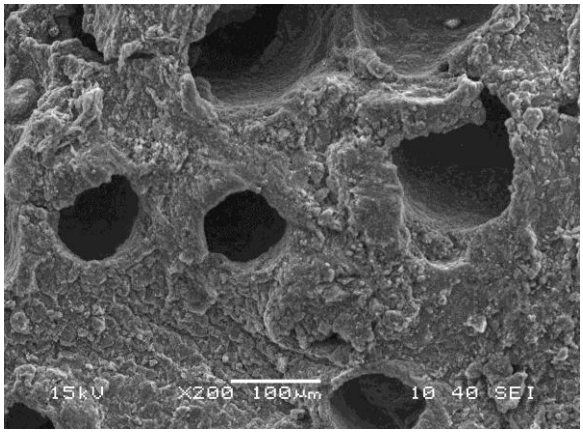


Fig 4.6 (a) SEM image of tyre char at (35X) Fig4.6 (b) SEM image of tyre char at (150X)



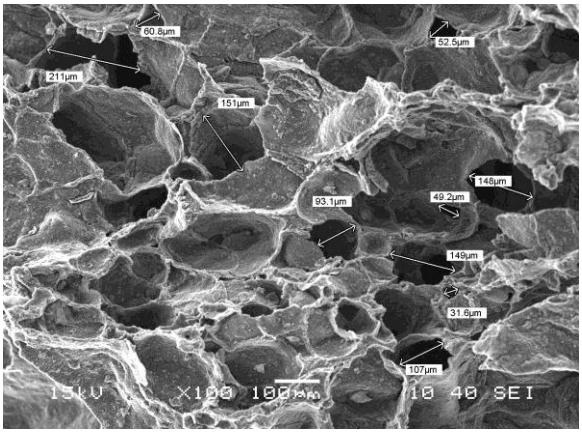
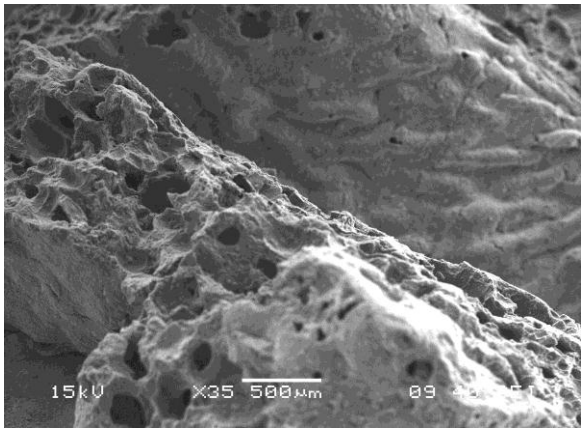
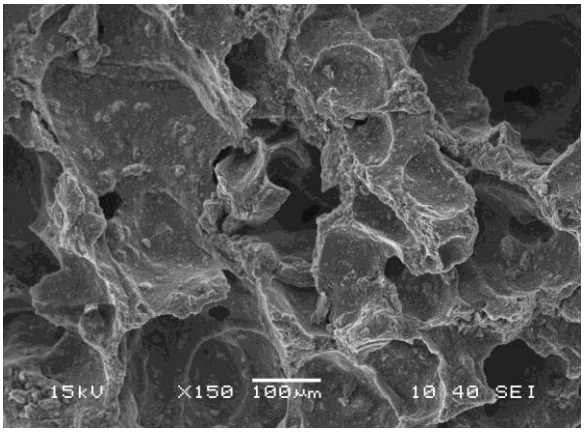
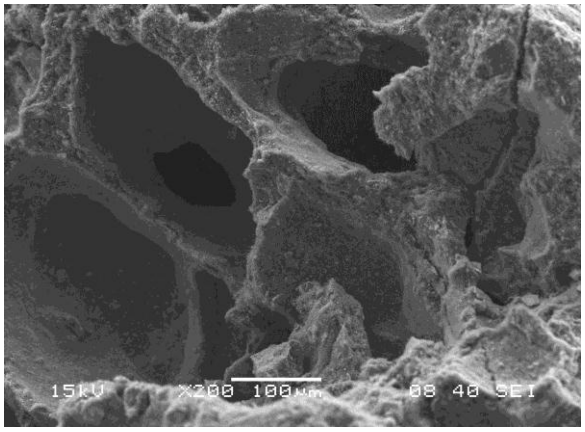


Fig 4.6 (c) SEM image of tyre char at (200X) Fig 4.6(d) SEM image of tyre char with pore





4.7(a) SEM image of tube char at (35X) Fig 4.7(b) SEM image of tube char at (150X)



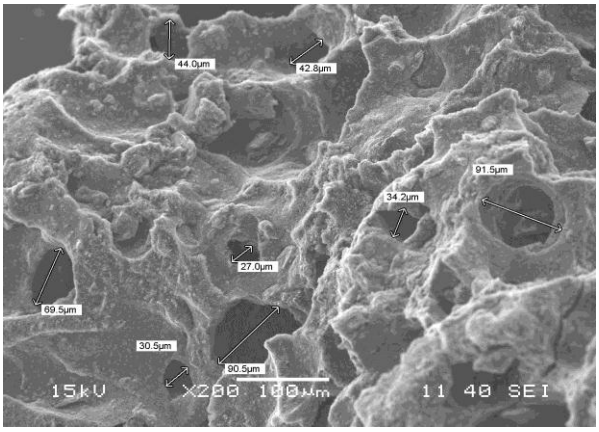


Fig 4.7(c) SEM image of tube char at (200X) Fig 4.7(d) SEM image of tube char with pore

CHAPTER 5

5. Kinetic Study

5.1 Introduction

Thermal behaviour of tyre and tube can be improved by knowing thermal degradation kinetics. So the kinetic study of waste tyre and tube pyrolysis provides a useful basis upon which to design a pyrolysis reactor. A thermogravimetric analysis (TGA) technique is an excellent way for studying the kinetics of thermal degradation. It provides information on pre-exponential factor and activation energy. When these polymeric materials subjected to heating or burning conditions, complicated reaction mechanism such as random-chain scission, end- scission, chain stripping, cross-linking and coke formation take place [24, 48]. The mechanisms of pyrolysis include a wide range of different reactions. Not every reaction causes the release of a volatile molecule. Some only cause a change in mechanical properties. During thermogravimetric analysis, only the weight loss is measured on heating, that means only those reactions causing the weight loss are considered. Furthermore, because of the system complexity, all reactions are lumped together into an overall reaction [7].

5.2 Mechanism and Calculation of Kinetic Parameters

TGA is used to find out the kinetic parameters in addition to the decomposition of tyre and tube comprises a large number of reactions in parallel and series, whereas TGA measures the overall kinetics rather than individual reactions. However, it is useful in providing comparative kinetic data under different reaction conditions such as temperature and rate of heating [45]. In this work first-order decomposition reaction with integral method was used to evaluate the kinetic parameters. The approach adopted by many researchers in kinetic analysis of TGA data for waste

materials is to assume first order reaction for devolatilization [49, 50, and 51]. So the first order reaction with respect to the amount of undecomposed material states that

A (Solids) → B (Solid) + C (Volatile) (1)

For 1st order reaction, we have:

$$dx/dt = k(1 - X) \quad (2)$$

$$k = k_0 * e^{(-Ea/RT)} \quad (3)$$

The extent of conversion or fraction of material pyrolyzed, X was defined by expression

$$X = (W_0 - W_t)/(W_0 - W_\infty)$$

Where W_0 is the initial weight (mg), W_t is the weight after "t" minutes (mg), and W_∞ is the weight after pyrolysis (mg).

Where R = Universal gas constant, 8.314J K^{-1} mol^{-1}

K_0= Pre-exponential factor (min^{-1}), and

E_a= Activation energy (KJ mol^{-1}) with linear heating rate of, A in K min^{-1}

$$A = {}^{dT}/_{dt} \quad (4)$$

Integrating Eq. (2) results in

$$\ln[-\ln(1 - X)] = \ln\left[\left(\frac{k_0 RT^2}{AEa}\right)\left(1 - \frac{2RT}{Ea}\right)\right] - {}^{Ea}/_{RT} \quad (5)$$

Fig 5.1, 5.2, 5.3 and Fig 5.4, 5.5, 5.6shows the kinetic Plots of ln[-ln(1-X)] against 1/T of tyre and tube at different heating rate should correspond to a straight line with a slope of (-Ea/R) giving the activation energy. And the pre-exponential factor also can be calculated by using activation energy and the intercept. Table 5.1 shows the trend line equations and regression coefficient which has been obtained from the graph with different phase of both tyre and tube. By using the corresponding equations and regression coefficient of three phases, activation

energy has been determined for both tyre and tube at different rates of heating and shown in Table 5.2 and Table 5.3.The average activation energy and pre-exponential factor of three phases has compiled in Table-5.4, From Table-5.4 it has been resulted that with increasing rate of heating, the activation energy was decreasing.

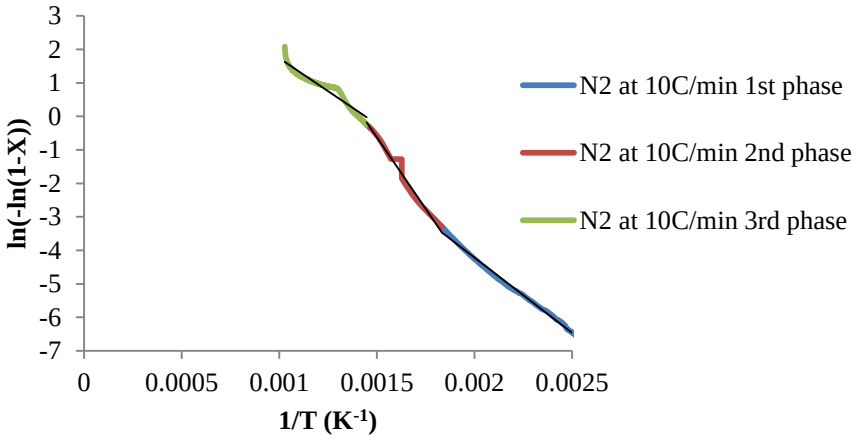


Fig 5.1 Kinetic graph of tyre at $10^{o}Cmin^{-1}$

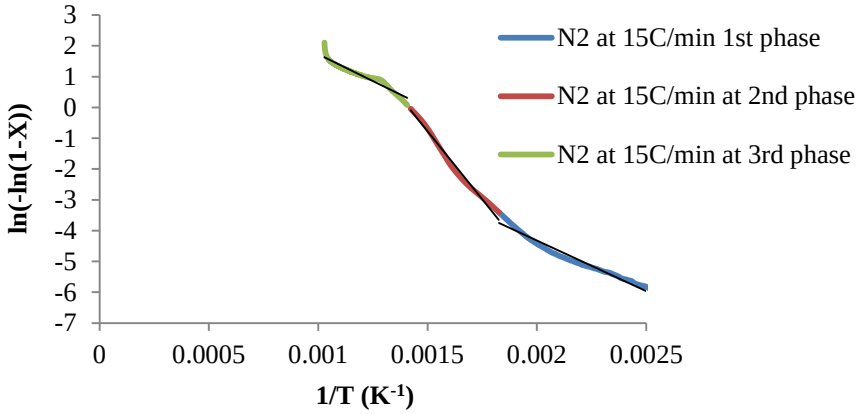


Fig 5.2 Kinetic graph of tyre at $15°Cmin^{-1}$

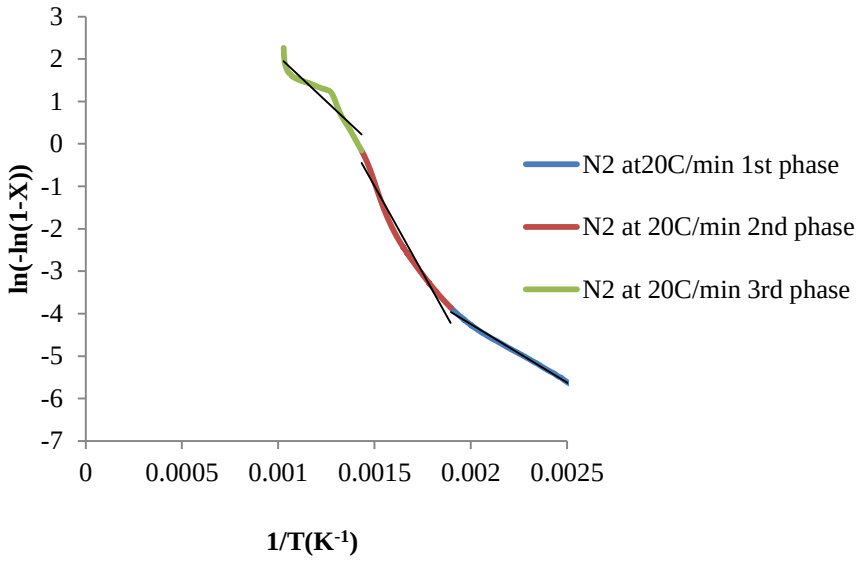


Fig 5.3Kinetic graph of tyre at 20°Cmin^{-1}

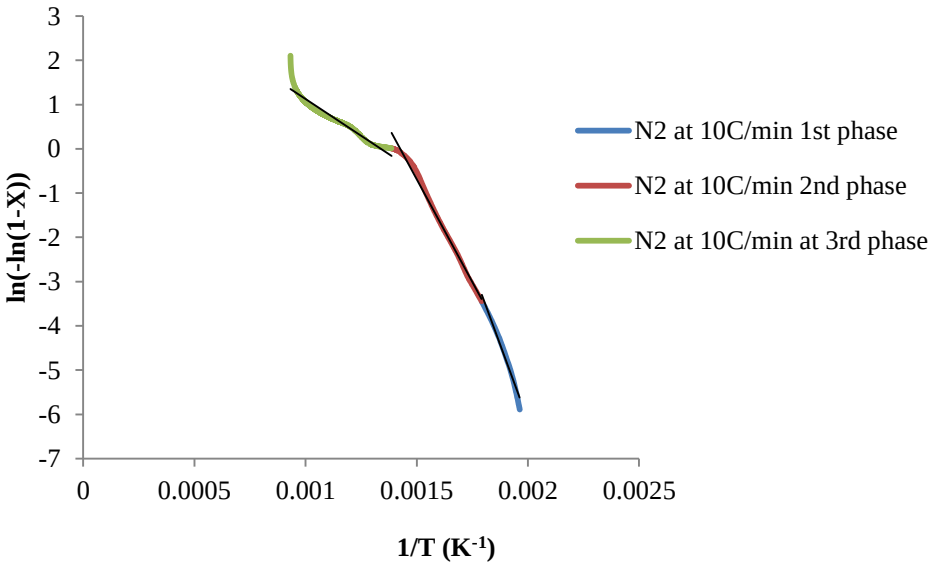


Fig 5.4 Kinetic graph of tube at 10 °C/min

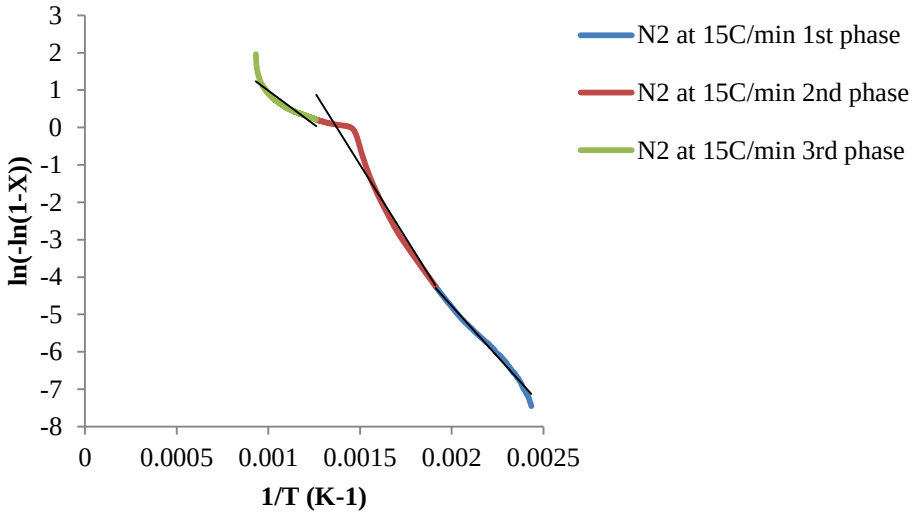


Fig 5.5 Kinetic graph of tube at 15°C/min

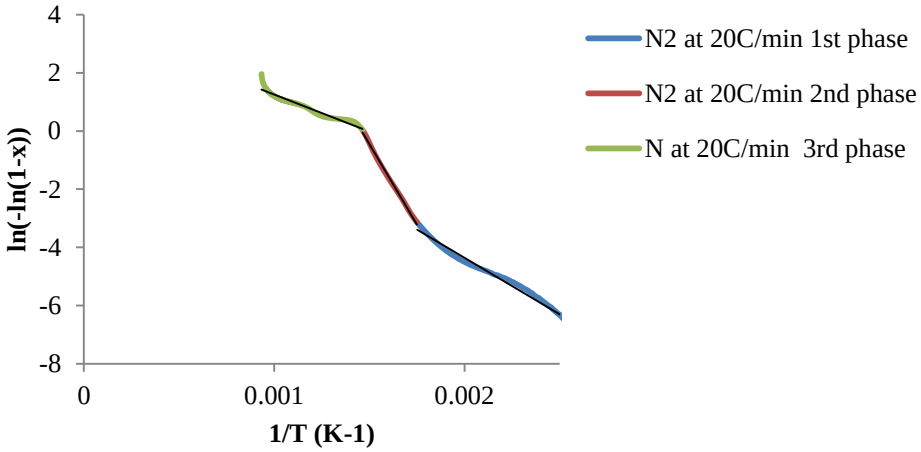


Fig 5.5 Kinetic graph of tube at 20°C/min

Table 5.1 Trend line equations and Regression coefficients of tyre/tube

Rate of heating	1St phase	2nd phase	3rd Phase
	Tyre sample		
10 °C min^{-1}	Y= -4485X+04.760 , R^2=0.996	Y= -8574X+12.24, R^2=0.984	Y= -3938X+5.676, R^2=0.932
15 °C min^{-1}	Y= -3285X+2.252, R^2=0.965	Y=-8822X+12.45, R^2=0.986	Y=-3494X+5.221, R^2=0.944
20 °C min^{-1}	Y=-2755X+1.261, R^2=0.997	Y=-8574X+12.24, R^2=0.984	Y=-4275X+6.344, R^2=0.893
	Tube sample		
10 °C min^{-1}	Y= -7859X+ 21.036 R^2=0.9829	Y=-9263X+13.20 R^2=0.990	Y=-3321X+4.4444 R^2=0.947
15 °C min^{-1}	Y=-5423.1X+6.076 R^2=0.993	Y=7829X+10.79 R^2=0.952	Y=-3647X+4.636 R^2=0.876
20 °C min^{-1}	Y=-3887X+3.415 R^2=0.981	Y=-6283X+16.16 R^2=0997	Y=-2557X+3.810 R^2=0.945

Table 5.2 Activation energy and pre-exponential factor of tyre

Rate of heating	Activation energy (KJ/Mol)		
	1st phase	2nd phase	3rd phase
10 °C min^{-1}	Ea= 37.28	Ea=71.28	Ea=32.74
15 °C min^{-1}	Ea=27.31	Ea=73.33	Ea=29.04
20 °C min^{-1}	Ea=22.90	Ea=71.28)	Ea=35.5
	Pre- exponential factor		
10 °C min^{-1}	7.10×10^9	1.3×10^9	4.73×10^9
15 °C min^{-1}	4.1×10^9	1.6×10^9	2.7×10^9
20 °C min^{-1}	1.3×10^9	4.7×10^9	1.0×10^9

Table 5.3 Activation energy and Pre-exponential factor of tube

Rate of heating	Activation energy (KJ/Mol)		
	1st phase	2nd phase	3rd phase
10 °C min^{-1}	Ea=65.33	Ea=77	Ea=27.61
15 °C min^{-1}	Ea=45.08	Ea=65	Ea=30.32
20 °C min^{-1}	Ea=32.31	Ea=52.23	Ea=21.25
	Pre- exponential factor		
10 °C min^{-1}	9.89×10^9	2.23×10^9	8.8×10^9
15 °C min^{-1}	3.16×10^9	2.4×10^9	1.26×10^9
20 °C min^{-1}	1.56×10^9	3.74×10^9	4.50×10^9

Table 5.4 Average activation energy and pre-exponential factor of tyre and tube

Rate of heating	Activation energy (KJ/Mol)	Pre exponential factor (K_0 min^{-1})
	Tyre sample	
10 °C min^{-1}	47.1	4.37×10^9
15 °C min^{-1}	43.22	2.8×10^9
20 °C min^{-1}	43.22	2.33×10^9
	Tube sample	
10 °C min^{-1}	56.64	6.97×10^9
15 °C min^{-1}	46.8	2.27×10^9
20 °C min^{-1}	35.26	3.26×10^9

5.3 Conclusion

From TGA, the value of I/T and ln[-ln(1-X)] has been calculated and plotted by splitting with three phases, three different activation energy has been obtained at different rate of heating. From Table 5.2 and Table 5.3, it was observed that at 2nd phase the activation energy is more forboth tyre and tube as compared to the 1st phase and 3rd phase. This may be due to the highest degradation of tyre and tube compound at 2nd stages so it required more energy for decomposition. Table 5.4 indicates the average of activation energy and pre-exponential factor of both tyre and tube, from the results it can be concluded that the obtained activation energy was decreasing with increasing rate of heating.

CHAPTER 6

6. Engine Performance Test

6.1 Introduction

Compression ignition engines are preferred prime movers due to their excellent drivability and higher thermal efficiency. Despite their advantages they produce higher levels of NOx and smoke which will have an effect on human health. Hence stringent emission norms have been imposed. In order to meet the norms and also the fast depletion of oil reserves have necessitated a search for alternate fuels for diesel engines. On the other hand, due to the rapid growth of automotive vehicles in transportation sector, the consumption of oil keeps increasing. And also, the disposal of used tyres from automotive vehicles becomes inexhaustible [52]. Though many of the research work has been done to develop the tyre oil from used tyre different recycling methods, however, alternative fuel from wastes such as plastic waste, tyre waste, and other solid waste is expected to play a major role in the ever-expanding transportation sector in the near future, specifically the on-road diesel engines subsector. Scientists around the world have explored several alternative energy resources, which have the potential to quench the ever-increasing energy thirst of today's population. These alternative energy resources are largely environment-friendly but they need to be evaluated on case-to-case basis for their advantages, disadvantages and specific applications. Some of these fuels can be used directly while others need to be formulated to bring the relevant properties closer to conventional fuels [53].From the research work it was proved that pyrolysis of waste automobile tyre chips produced pyrolysis oil, pyrolysis gas and char, it also reported that TPO (Tyre pyrolysis oil) has properties similar to that of DF (diesel fuel) [54]. As a result in the recent years some experimental studies investigated that use of TPO derived from waste automobile tyres can be used as an alternate fuel in diesel

engine. *Murugan S et al.* has carried out the performance and emission characteristics of a single cylinder direct injection diesel engine fuelled by 10, 30 and 50 percent blends of tyre pyrolysis oil (TPO) with diesel fuel (DF) [55]. Results showed that the brake thermal efficiency of the engine fuelled by TPO-DF blends increased with increase in blend concentration and higher than DF. NOx, HC, CO and Smoke emissions were found to be higher at higher loads due to high aromatic content and longer ignition delay. The cylinder peak pressure increased from 71.4 bar to73.8 bar. The ignition delays were longer than DF. Studies have been carried out the possibility of using wood pyrolysis oil as an alternate fuel in internal combustion engine [56, 57]. Reliable operation was recorded with wood pyrolysis oil-diglyme blends without any modification in the engine.

The crude tyre pyrolysis oil was desulphurised and distilled to improve the properties and studied the performance, emission and combustion characteristics of it on a single cylinder four-stroke air cooled engine fuelled with two different blends, 30% tyre pyrolysis oil and 70% diesel fuel (TPO 30) and 30% distilled tyre pyrolysis oil and 70%diesel fuel (DTPO 30). The results of the studies indicated that NOx is reduced by about 8% compared to tyre pyrolysis oil and by about 10% compared to diesel fuel. Hydrocarbon emission is reduced by about 2% compared to TPO 30 operation. Smoke increased for DTPO 30 compared to TPO 30 and diesel fuel [58].

The present work is based on engine performance test by using bicycle tube pyrolytic oil. The tube pyrolytic oil was obtained at a temperature range of 700°C by using batch reactor. The performance, emission and combustion characteristics of the diesel engine was studied by using 10%, 20%, 30%, 40%and 50% of tube pyrolytic oil blend with diesel.

6.2 Experimental Setup

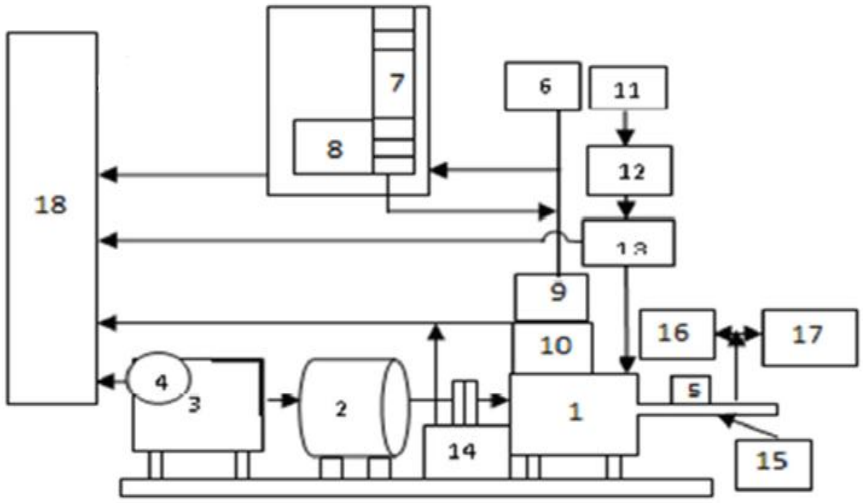


Fig-6.1Schematic diagram of the engine experimental setup

1	Engine	10	Fuel pump
2	Alternator	11	Air filter
3	Control panel	12	Air box
4	Load switch	13	Air flow sensor
5	Thermocouple	14	Speed sensor
6	Fuel tank	15	Exhaust pipe
7	Burette	16	Gas analyser
8	Fuel sensor	17	Smoke meter
9	Fuel filter	18	Computer with data acquisition system

6.2.1 Engine specification

KIRLOSKAR TAF 1 model engine, with brake power 4.4 KW, 1500 rpm rated speed, and has a compression ratio 17.5:1 was used and specifications are given in Table-6.1

Table 6.1Engine specification

Make/Model	Kirloskar TAF 1
Brake power, kW	4.4
Rated speed, rpm	1500
Bore [mm]	80
Stroke [mm]	110
Compression Ratio	17.5:1
Nozzle Opening Pressure [bar]	200
Injection Timing [^{o}CA]	23

6.3 Results and discussion

6.3.1 PERFORMANCE CHARACTERSTICS

6.3.1.1 Brake Thermal efficiency

The variations of brake thermal efficiency with brake power of different blends of tube pyrolytic oil (TUPO) and diesel is presented in Fig 6.2. It was observed that, there was a gradual increase in brake thermal efficiency with increases in brake power. Brake thermal efficiency of diesel fuel increased from17.14 to 30.48% with increase in load. For 40% blend of TUPO at full load a maximum brake thermal efficiency of 32.58 was observed. The percentage increase in brake thermal efficiency was 6.8% when compared to diesel fuel. The increase in brake thermal efficiency may be due to the lower viscosity of the blend which leads to better fuel atomization and combustion [59], The results are tabulated in Table 6.2.

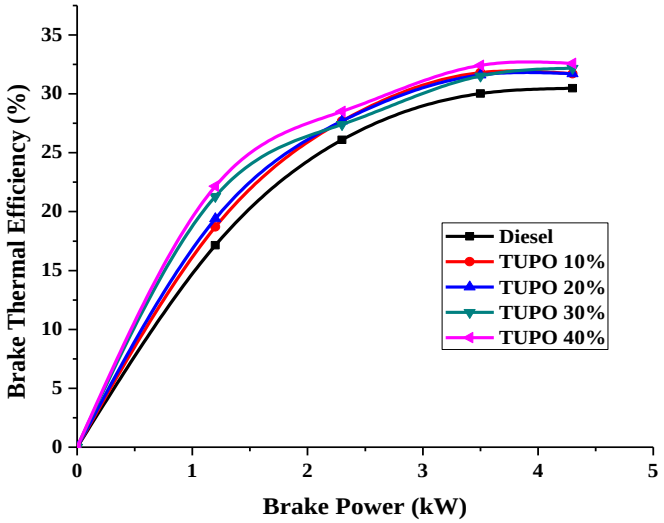


Fig 6.2 Variation of BTE with brake power

Table 6.2 Results of variation of BTE with brake power

Brake Power (kW)	Brake thermal Efficiency (%)				
	Diesel	10	20	30	40
0	0	0	0	0	0
1.2	17.14	18.7	19.4	21.3	22.71
2.3	26.1	27.7	27.7	27.4	28.5
3.5	30.02	31.6	31.6	31.52	32.42
4.3	30.48	31.7	31.7	32.17	32.58

6.3.1.2 Brake Specific Energy Consumption

Brake specific energy consumption (BSEC) is more reliable criteria compared to brake specific fuel consumption for comparing fuels having different calorific values and densities. This specific energy consumption measures the amount of input energy required to develop one kilowatt power. The brake specific energy consumption of a blended fuel is the product of

the brake fuel consumption and calorific value of the corresponding blend. Fig 6.3, illustrates the variation of energy consumption for different blends of TUPO and diesel fuel with brake power. The brake specific energy consumption of TUPO blends decrease with increase in load and also it is lower than that of diesel fuel. BSEC at TUPO10% blend was found to be 11.14 MJ/kW hr at full load which was less than that of 20%, 30% and 40% blends, these values are shown in Table 6.3.This may be due to faster burning rates and more heat release rate of TUPO blends [60]. It is an important parameter to compare brake thermal efficiency of an engine because it is taking care of both mass flow rate and heating value of fuel [61].

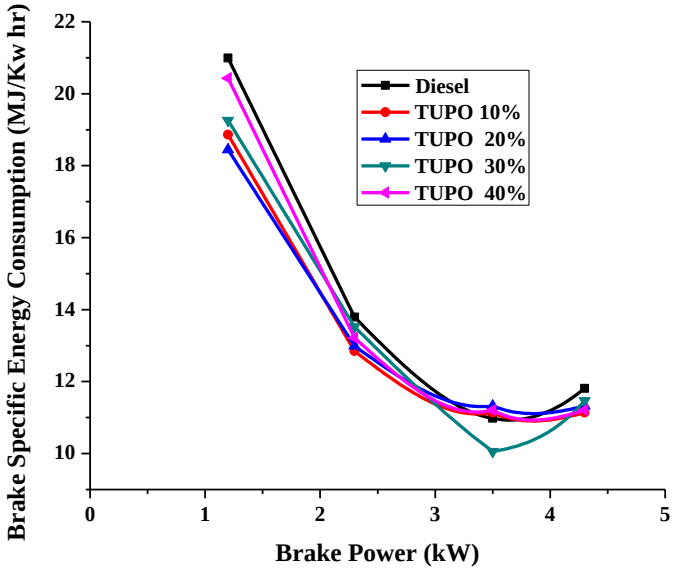


Fig 6.3 Variation of BSEC with brake power

Table 6.3 Results of variation of BSEC with brake power

Brake Power (kW)	Brake Specific Energy Consumption (Mj/kW hr)				
	Diesel	10	20	30	40
0	nd	nd	nd	nd	Nd
1.2	20.99	18.86	18.44	19.26	20.43
2.3	13.79	12.85	12.99	13.52	13.22
3.5	10.89	11.14	11.32	10.06	11.21
4.3	11.81	11.14	11.32	11.47	11.21

6.3.1.3 Exhausts gas temperature

Fig 6.4shows the variations of exhaust gas temperature (EGT)at different load. In general EGT increased with increase in engine load for all the fuel tested. The EGT increased linearly from 119 °Cat no load to 308 °C at full load condition for 20% blending of TUPO. This increase in EGT with load is obvious from the simple fact that more amount of fuel was require din the engine to generate that extra power needed to take up the additional loading [62, 63]. Another reason for the increased EGT may be due to heat release in the later part of combustion because of the presence of higher molecular weight compounds in the fuel blends that do not brake easily during the actual combustion process [64]. Exhaust gas temperature are shown in Table 6.4

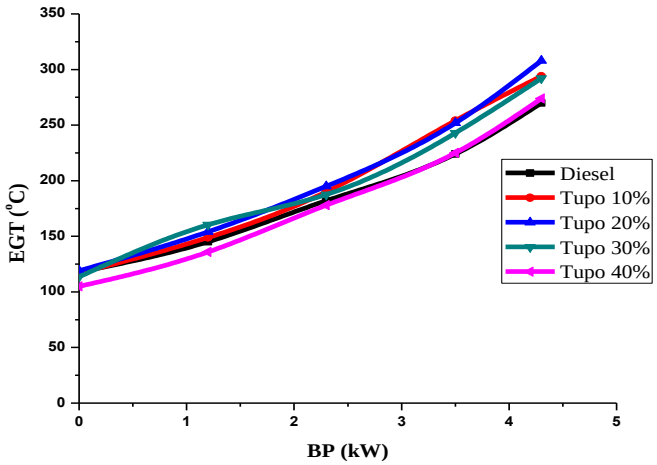


Fig 6.4 Variation of EGT with Brake power

Table 6.4 Results of variation of EGT with brake power

Brake Power (kW)	Exhaust gas temperature (°C)				
	Diesel	10	20	30	40
0	118	117	119	113.6	105
1.2	145	149	154	160.3	136
2.3	182	190	195	187.6	178
3.5	224	254	252	243	225
4.3	270	294	308	292	274

6.3.2EXHAUST EMISSIONS

6.3.2.1 Carbon Monoxide (CO) emissions

When petroleum based fuels burn in an engine the main toxic substances present in the waste gases in exhaust are incomplete oxides of hydrocarbon containing CO, HC, CO_2. Carbon monoxide (CO) emission is the most toxic substance found in exhaust gases. HC and CO emissions are the main products of incomplete combustion. Fig 6.5 shows the variation of carbon monoxide emission of tube pyrolytic oil with brake power. Generally, CI engine operates with lean mixtures and hence the CO emission would be low [65]. From the figure it is clear that for 10% blend of TUPO, CO emissions is somewhat higher at low loads compared with that of diesel. The reason for the increase of CO emission may be incomplete combustion due to reduce in-cylinder temperatures [66]. Higher emission values of CO can be attributed to the poor mixture preparation, inefficient combustion due to higher viscosity and poor volatility. At 30%and 20 % blending the CO emission is less because tube pyrolytic oil mixtures contain some extra oxygen that resulted in complete combustion of the fuel and supplied the necessary oxygen to convert CO to CO_2[67]. The volume percentage of CO is shown in Table 6.5.

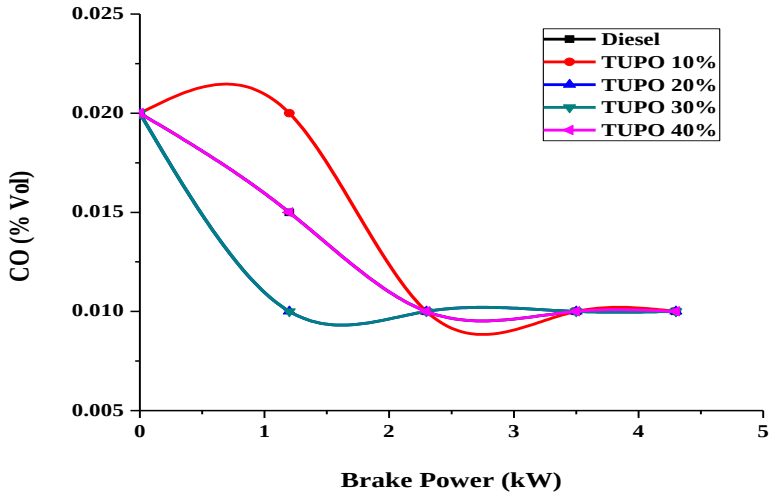


Fig 6.5 Variation of CO with brake power

Table 6.5 Results of variation of CO with brake power

Brake Power (kW)	CO (% Volume)				
	Diesel	10	20	30	40
0	0.02	0.02	0.02	0.02	0.02
1.2	0.015	0.02	0.01	0.01	0.015
2.3	0.01	0.01	0.01	0.01	0.01
3.5	0.01	0.01	0.01	0.01	0.01
4.3	0.01	0.01	0.01	0.01	0.01

6.3.2.2 Hydrocarbon emissions

Fig 6.6 shows that hydrocarbon emission for different blends of tube pyrolytic oil compared with diesel fuel. Unburned hydrocarbon is a useful measure of combustion inefficiency. Unburned hydrocarbon consists of fuel that is incompletely burned [66].HC emission varies from 22 ppm at no load to 14 ppm at full load for diesel fuel and for TUPO 10, TUPO 20, and TUPO 30 and TUPO 40 HC emissions varied from 18, 18, 17, and 16 ppm at no load to 10, 11, 11 and 12 at full load condition (Table 6.6).Decreased flame quenching thickness is the reason for the reduction in unburned hydrocarbons [68]. On the other hand it was explained by *Mani etal*.at lighter loads due to charge homogeneity and higher oxygen availability, the unburned hydrocarbon level is less, whereas at higher load ranges due to higher quantity of fuel admission, unburned hydrocarbon increases [66]. From the figure it is clear that engine emits more HC for diesel at part load conditions when compared to other blends.

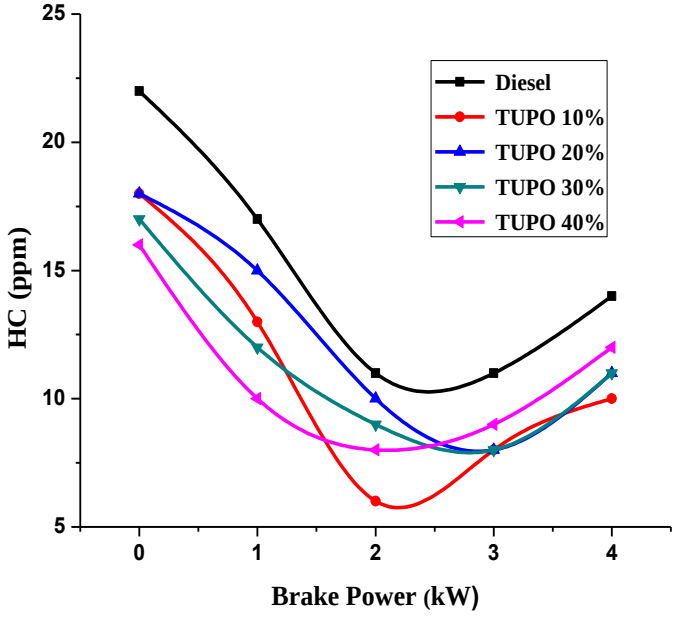


Fig 6.6 Variation of HC with brake power

Table 6.6 Results of variation of HC with brake power

Brake Power (kW)	Hydrocarbon (ppm)				
	Diesel	10	20	30	40
0	22	18	18	17	16
1.2	17	13	15	12	10
2.3	11	6	10	9	8
3.5	11	8	8	8	9
4.3	14	10	11	11	12

6.3.2.3 Carbon di-oxide (CO_2) emissions

Carbon dioxide occurs naturally in the atmosphere and is a normal product of combustion [69]. The emission levels of CO_2 for various blends of TUPO and diesel is shown in Fig 6.7.The results revels that the CO_2 emissions gradually increased with increasing brake power. CO_2 emissions are higher in the case of TUPO 40% blend at full load and remaining blends shows lesser CO_2 emissions; however the CO_2 emissions of the TUPO blends were lower than that of

diesel fuel. The increase of CO_2 emission at full loads is due to the higher fuel entry. Generally it contains lower carbon content as compared to diesel and hence the CO_2 emissions are comparatively lower than diesel. The volume percentage of CO_2 with brake power is given in Table 6.7

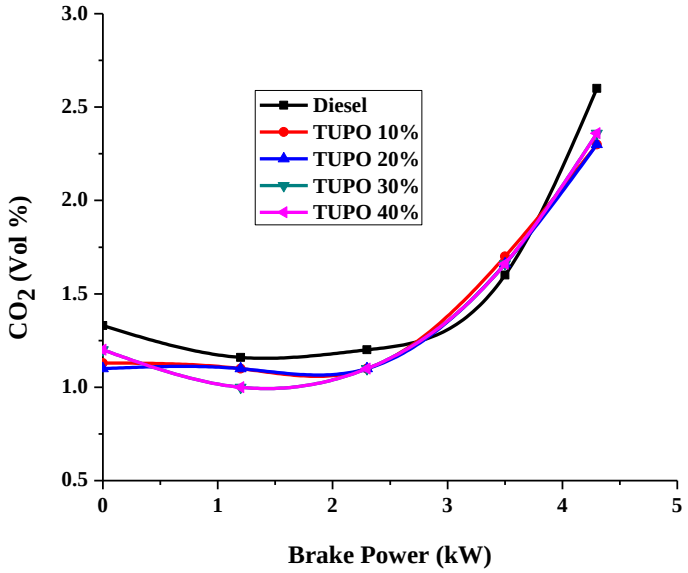


Fig 6.7 Variation of CO_2 with Brake power

Table 6.7 Results of variation of $CO_2$with brake power

Brake Power (kW)	CO_2 (Volume %)				
	Diesel	10	20	30	40
0	1.33	1.13	1.1	1.2	1.2
1.2	1.16	1.1	1.1	1	1
2.3	1.2	1.1	1.1	1.1	1.1
3.5	1.6	1.7	1.66	1.66	1.66
4.3	2.6	2.3	2.3	2.32	2.36

6.3.2.4 NO_X Emissions

Fig 6.8shows the comparison of NOx emission with brake power for the tested fuels. The formation of NOx is highly dependent on in-cylinder temperature, oxygen concentration and residence time for the reactions to take place [70]. It can be observed from the figure that there was a gradual increase in NOx emission with increase in the blend concentration but lesser than that of diesel fuel. Due to higher heat release rates there is an increase in cylinder temperature resulting in increase in NOx emissions [65]. The in-cylinder temperature has a strong effect on the formation of NOx. If the combustion temperature is higher, then higher NO_X is formed [66]. The NOx emissions for TUPO10% blend at full load are 459 ppm and for diesel fuel it was 502 ppm (Table 6.8). For all the TUPO blends the NOx emissions were lower than diesel fuel.

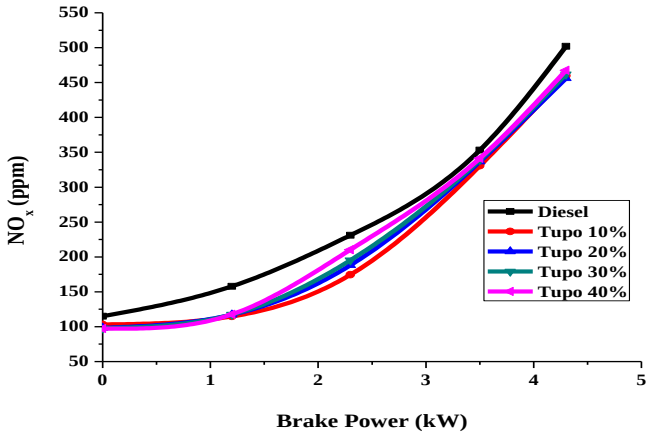


Fig 6.8 Variation of NO_x with Brake power

Table 6.8 Results of variation of NOx with brake power

Brake Power (kW)	NOx (ppm)				
	Diesel	10	20	30	40
0	115	103	98	97	97
1.2	158	114	117	117	117
2.3	231	174	188	195	210
3.5	353	330	336	339	341
4.3	502	459	456	461	467

6.3.3 COMBUSTION CHARACTERISTICS

6.3.3.1 Ignition delay

Ignition delay is the length of time or number of degree of crankshaft rotation between the beginning of injection and ignition of fuel. It is observed from the figure that the ignition delay of all the fuels tested decreased with increase in engine load. The ignition delay values of TUPO blends and diesel are 11.3°CA, 12.1°CA, 11.89°CA, and 11.6°CAat full load of 10%, 20%, 30% and 40% blend, 12.69°CA at full load of diesel (Table 6.9), and it is lower than that of diesel fuel. The reason for this shorter ignition delay was due to the chemical reactions led to the formation of gases of lower molecular weight on the peripheral region with a very dense inner core of oils of higher molecular weight. Rapid vaporization of this lighter oil in the fringe of the spray spread out the jet and thus volatile combustible compounds ignited earlier and reduced the delay period [71].

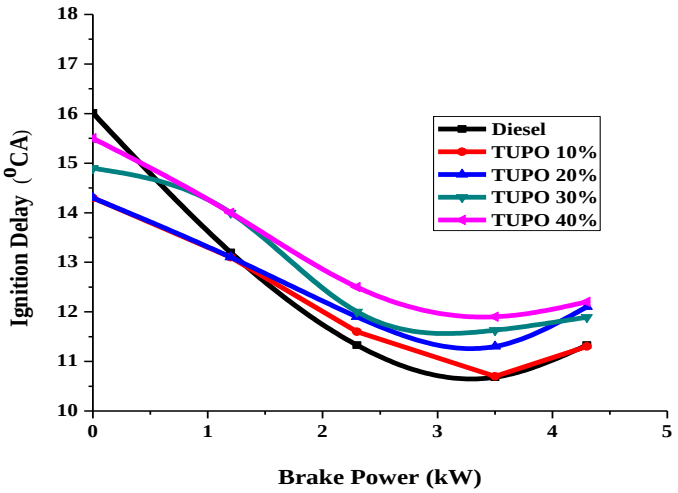


Fig 6.9 Variation of Ignition delay with brake power

Table 6.9 Results of variation of Ignition delay with brake power

Brake Power (kW)	Ignition delay (°CA)				
	Diesel	10	20	30	40
0	16.01	14.3	14.3	14.9	15.5
1.2	13.2	13.1	13.1	14	14
2.3	11.33	11.6	11.9	12	12.5
3.5	10.68	10.7	11.3	11.63	11.9
4.3	11.33	11.3	12.1	11.89	12.2

6.3.3.2Maximum cylinder pressure (Pmax)

Fig 6.10 shows the variation of maximum cylinder pressure (Pmax) with engine load. The peak cylinder pressure increases with increase in load as the engine gains more heat .It is a measure of the amount of fuel accumulated during the delay period that takes part in the premixed combustion phase. The peak pressure values of TUPO blends are higher than diesel fuel. At full load the Pmax value for diesel is 75.7 bar whereas for TPO blends the values are 78.3bar, 78.96bar and 79.08bar (Table 6.10) respectively for TPO10, TPO20 and TPO30 which are higher than diesel. Higher heat release rate may be the reason for higher peak pressure [72].

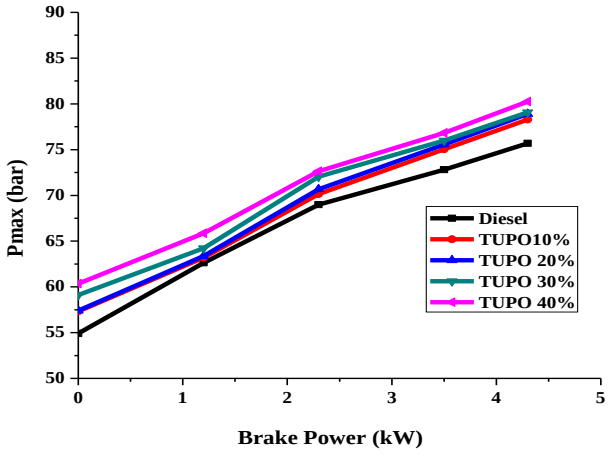


Table 6.10 Results of variation of Pmax with brake power
Fig 6.10 Variation of Pmax with brake power

Brake Power (kW)	Maximum cylinder pressure (Pmax)				
	Diesel	10	20	30	40
0	54.91	57.31	57.41	59.1	60.35
1.2	62.62	63.19	63.36	64.23	65.86
2.3	68.99	70.15	70.67	72.05	72.63
3.5	72.81	75.03	75.55	76	76.82
4.3	75.7	78.3	78.9	79.08	80.25

6.4 Conclusion

Following are the major conclusions drawn from the experimental work conducted with diesel and waste tube pyrolytic oil blend on diesel engine.

- It is observed that engine is able to run up to 40% of TUPO. Engine failed to run satisfactorily with 50% blend of TUPO.
- Brake thermal efficiency increases with increase in brake power and the percentage increase in brake thermal efficiency was 6.8% for TUPO at 40% blend when compared to diesel fuel.
- Brake specific energy consumption decreases with increase in load and less than that of DF. At 40% blend the brake specific energy consumption decreases by 5% for TUPO.
- For 10% blend of TUPO, CO emissions are somewhat higher at low loads compared with that of diesel.
- HC, CO, CO_2 and NOx emissions were found lower than that of diesel.
- The peak pressure values of TUPO blends are higher than diesel fuel. At full load the Pmax value for diesel was 75.7 bar whereas for TUPO 40% blends the value was 80.25 bar.
- From the above, it can be concluded that 40% blend of tube pyrolytic oil with diesel can be substituted with diesel.

CHAPTER-7

7. Conclusion and Future Scope

7.1 Conclusion

In this research, the recovery of value added products from waste tyre and tube pyrolysis were investigated. Both thermal and catalytic pyrolysis of waste tyre and tube has been studied. The thermal pyrolysis has been carried out in a semi-batch reactor under different temperature ranges from 450°C to 700°C for tyre and 450°C to 800°C for tube and following conclusions were observed.

- The maximum yield of oil obtained was 49.6% and 49.65% at an optimum temperature of 600°Cfor tyre and 700°C for tube respectively.
- It was also observed that with increase in temperature both oil and gas was increased. This is due to the strong cracking of tyre rubber and the secondary cracking takes place inside the reactor. But the char yield was decreased with increase in temperature. This shows the effect of temperature on production yield.
- By comparing thermal and catalytic pyrolysis it is concluded that the maximum oil yields can be obtained in thermal pyrolysis as compared to catalytic pyrolysis.
- Obtained physical properties of both tyre and tube pyrolytic oils were exist in between the range of diesel and gasoline. It seems the pyrolytic oils were mixture of diesel and gasoline.
- It is concluded from GC-MS and FTIR analysis that the chemical composition and the functional groups present in both the pyrolytic oil were that of aromatics and aliphatic compounds. From GC-MS analysis the tyre and tube pyrolysis contains around 30 chemical compounds of varying carbon chain length from C_6-C_{17} and C_8-C_{17} respectively.

- From the kinetic study it was proved that kinetic study of the thermal degradation of waste tyre and tube showed that with increase in rate of heating the activation energy is decreased.
- Engine performance test by using bicycle tube pyrolytic oil has shown the performance, emission and combustion characteristics of the diesel engine by using 10%, 20%, 30%, 40%and 50% of tube pyrolytic oil blend with diesel. And it concluded that the brake thermal efficiency increases with increase in brake power.
- Emission characteristics of TUPO in engine test show that all the emissions are lower than that of diesel.
- The peak pressure values of TUPO blends are higher than diesel fuel.
- From engine test it was concluded that above 40% blend the diesel engine was not running smoothly and it produces poor result. So 40% was the optimum blend to run the diesel engine.
- By considering all these results, it can be concluded that the oil obtained from pyrolysis of waste tyre and tube can be used as alternative fuel after proper treatment.

7.2 Future Scope

- Better experimental model can be made to improve the quality and quantity of products.
- Different catalysts or modification of the catalysts can be used to obtain more yields of the oil products.
- Fractionating columns can be used for separation of the oil fuel into different fractions.
- Different kinetic methods and models can be used for designing a suitable reactor to maximize the oil product.
- Optimization of the process to achieve an economical and eco-friendly method.

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Journal:

1. Debalaxmi Pradhan, R.K. Singh, "Characterization of the Liquid Product obtained by Pyrolysis of bicycle Tube" accepted in Energy Sources, Part-A, Recovery, Utilization, and Environmental Effects.

2. Debalaxmi Pradhan, R.K.Singh, "Thermal Pyrolysis of bicycle waste Tyre Using Batch Reactor"accepted in International Journal of Chemical Engineering and Applications.

Conferences:

1. Debalaxmi Pradhan, R.K. Singh, "Conversion of liquid fuel from waste PVC",19-21 December 2009 held at NIT Rourkela, India.

2. Debalaxmi Pradhan, R.K. Singh, "Influence of temperature on product distribution by pyrolysis of scrap bicycle tyres", International conferences on recent advanced in chemical engineering and Technology (RACET 2011), 10-13th March 2011 held at Kochi, India.